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ATMOSPHERIC INPUTS OF PHOSPHORUS TO SOUTHERN LAKE HURON, APRIL-OCTOBER 1975

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FOREWORD

Our nation's freshwaters are vital for all animals and plants, yet our diverse uses of water---for recreations, food, energy, transportation, and industry---physically and chemically alter lakes, rivers, and streams. Such alterations threaten terrestrial organisms, as well as those living in water. The Environmental Research Laboratory in Duluth, Minnesota develops methods, conducts laboratory and field studies, and extrapolates research findings

--to determine how physical and chemical pollution affects aquatic life

--to assess the effects of ecosystems on pollutants

--to predict effects of pollutants on large lakes through use of models

--to measure bioaccumulation of pollutants in aquatic organisms that are consumed by other animals, including man.

This report evaluates the relative contributions of wetfall and dryfall to the total atmospheric input of phosphorus to the southern portion of Lake Huron. Airborne and other non-point sources can account for a significant amount of pollutants coming into an ecosystem. These must be considered when assessing the total impact of a pollutant on a body of water.

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ABSTRACT

The input of phosphorus has been demonstrated to be seasonally dependent. Of the total input, approximately half is potentially available, and one-fourth is immediately available. Inputs due to wet and dry deposition are roughly equal in magnitude. The major source appears to be agriculture with at least 10% due to combustion sources. A model for particulate deposition was used to determine the deposition velocity of phosphorus containing particles. The value of 0.6 cm/sec is considered applicable to other components whose mean diameter is 1μm.

CONTENTS

	Page
Foreword	iii
Abstract	iv
Figures	vi
Tables	vii
Acknowledgments	viii
Section:	
1. Introduction	1
Objectives	1
Definitions	2
2. Conclusions and Recommendations	3
3. Procedures and Methods	5
Equipment	5
Sampling	6
Sample Preparation and Chemical Analysis	7
Meteorological Data	9
4. Results and Discussion	14
Total Fallout	14
Wet Deposition	16
Total Aerosol Loading	19
Aircraft Sampling	22
Aerosol Samples	25
Particle Size Distribution of Phosphorus	28
Determination of Deposition Velocity	29
5. Total and Relative Inputs of Phosphorus from Wet and Dry Deposition	46
Wet Deposition	46
Dry Fallout	47
Total Deposition	47
Literature Cited	49
Appendix	51

FIGURES

Number		Page
1	Location of sampling devices aboard the ROGER B. SIMONS	6
2	Location of sampling and meteorological stations	8
3	Wind speed, direction and aerosol concentration roses	11
4	Monthly variation of available phosphorus in integrated fallout samples	16
5	Comparison of rainfall, concentration of reactive phosphorus in rain and total available phosphorus collected in integrated samples, April-October 1975	18
6	Relationship between total aerosol concentration, soluble and available phosphorus	21
7	Flight paths for aircraft sampling, 15-17 September 1975	23
8	Plots of backscatter vs. altitude	26
9	Monthly aerosol total available phosphorus concentration	29
10	Size distribution of phosphorus in aerosol samples collected from April through September 1975	36
11	Plot of aerosol available phosphorus for each station, April-October 1975	39
12	Deposition (C/Co) vs. wind speed	43
13	Schematic representation of mixing box model for particle deposition	43
14	Deposition velocity, Vd, vs. wind speed	44

TABLES

Number		Page
1	Comparison of R/V ROGER R. SIMONS and National Weather Service data on wind direction	16
2	Integrated fallout samples-volume collected and available phosphorus content, 1975	15
3	Comparison of observed and calculated rainfall	17
4	Phosphorus content of event rain samples, June-October 1975	19
5	HiVol loadings, June-October 1975	20
6	Aircraft particulate sample summary	24
7	Analysis of aerosol samples for soluble, reactive, and bound phosphorus content	27
8	Average monthly aerosol phosphorus concentration	28
9	Aerosol concentration of soluble and reactive phosphorus by station for the months April-October 1975	30
10	Size distribution of phosphorus-containing particles, April-September 1975	37
11	Calculation of deposition velocity at various wind speeds	44
12	Wet, dry and total available phosphorus deposition for the months of April-October 1975	46

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Our thanks are also extended to James V. Murphy, Captain of the R/V ROGER R. SIMONS, and his crew for their help in collecting over-the-lake samples; to Chas. Fitzsimmons of the EPA-National Environmental Research Center, Las Vegas, Nevada, and his crew for collecting the aircraft samples; and to C. Robert Snider of the U.S. Weather Service Forecast Office, Detroit Metropolitan Airport, for supplying the meteorological data.

The dedicated work of Barbara Kure, Isaac Walden and Jane Matthews in collecting the samples under sometimes gruelling conditions accounted for the success of the sampling scheme. Our thanks are also extended to Jill Goodell, who performed the majority of the chemical analyses. Finally, the helpful suggestions of and stimulating discussions with John Robbins, Great Lakes Research Division, and Donald Stedman, Atmospheric and Oceanic Sciences, University of Michigan, must be acknowledged as valuable aids to the program.

SECTION I

INTRODUCTION

Upon completion of the Port Huron water tunnel, the southern portion of Lake Huron will serve as the principal water supply for the Metropolitan Detroit/Windsor and Port Huron/Sarnia areas. The quality of this water is therefore important, and any adverse changes which may occur must be anticipated and, if possible, prevented. To do so, a knowledge of chemical species which can affect water quality is necessary.

Phosphorus has been determined to be the limiting nutrient in the Great Lakes system (Schelske & Stoermer 1971, 1972; Schelske et al. 1972; Miller et al. 1974) and therefore inputs and rates of phosphorus should be routinely monitored. It has been estimated that atmospheric inputs may account for up to 30% of the phosphorus and nitrogen entering Lake Superior (Elder 1975). In a study of the dissolved, suspended and scavenged phosphorus in precipitation in the southern portion of Lake Michigan, Murphy (1974) concluded that wet deposition alone accounts for 20-11% of the available phosphorus entering the lake. If the input due to dry fallout had been considered, this value would have been significantly higher.

It should be noted that all of the phosphorus entering the lake from the air must pass through the layer of maximum biological activity (euphotic zone). This is not true of river or lakewater inputs. Further, since dissolved phosphorus in rain provides an immediate but intermittent source of nutrient to the biomass whereas dry fallout provides a continuous source, the effect of each type of atmospheric input must be evaluated.

OBJECTIVES

The principal objective of this investigation was to determine the total input of phosphorus to the southern portion of Lake Huron from the atmosphere. This was achieved through the monthly collection and analysis of total integrated fallout samples from 11 shore-based sampling stations. The relative inputs of wet and dry fallout were determined by collection and analysis of event rain samples and filtered particulate samples from the shore-based and shipboard stations.

The majority of the work, however, involved the determination of the input to the lake from dry fallout. This area has received little attention in the past, due in part to the difficulty involved in collecting meaningful data. To accomplish this objective, aerosol samples were collected from shore-based, shipboard and aircraft-mounted sampling equipment. This intensive investigation has resulted in a significant increase in the knowledge of

dry deposition over lake surfaces.

DEFINITIONS

Total Soluble Phosphorus is defined as the amount of phosphorus (as orthophosphate, PO_4^{-3}) in neutral unbuffered samples. For aerosol samples, it is the amount of phosphorus (as PO_4^{-3}) obtained from complete extraction of a filter with distilled water. Total Reactive Phosphorus refers to the amount of phosphorus (as PO_4^{-3}) extracted with pH 7 sulfuric acid from a sample which has been previously extracted with distilled water. Total Available Phosphorus is the sum of the soluble and reactive phosphorus. In the integrated fallout samples, total available phosphorus was determined by analysis of the acidified sample after filtration through glass fiber mats to remove turbidity due to undissolved particles. Since these samples were pre-acidified, total soluble phosphorus values could not be obtained; therefore, for comparison of aerosol and integrated fallout samples, total available phosphorus values were used. Total Phosphorus values were obtained by digestion of samples in a persulfate/sulfuric acid medium and this term refers to the sum of all phosphorus in the sample, including soluble, reactive, inorganic- and organic-bound phosphorus. Samples are referred to by the method of collection, e.g., Andersen, HiVol and Gelman refer to aerosol samples collected by Andersen cascade impactors, high volume samplers, and Gelman Air Sampling Kits, respectively.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

This one-year duration study has differentiated between wet and dry atmospheric inputs and has determined 3 types of phosphorus entering the lake, based on potential impact on the lake. This approach has been shown to be superior to the collection of total integrated fallout samples that are subject to contamination from local sources and do not accurately reflect the input over the open lake. Due to chemical changes in fallout samples which occur during the collection period, the actual form in which the chemical species would have entered the lake is not known. Using integrated fallout collectors, the rate of available phosphorus input to the lake was determined to be 6.3 ng/cm^2/dy, which is approximately one-third of the total atmospheric input to the lake. This is significantly higher than the sum of the wet (2.2 ng/cm^2/dy) and the dry input (1.7 ng/cm^2/dy). For both wet and dry inputs, approximately 1/4 of the total input of phosphorus is immediately soluble and half is potentially available. During periods of reduced biological activity, the sum of wet and dry depositions accounts for 73% of the amount observed from integrated fallout collectors, however. Both types of phosphorus input are seasonally dependent, being highest in the spring and fall. On the basis of this and from total atmospheric loading and the particle size distribution of the phosphorus-containing particles, it has been concluded that a majority of the phosphorus inputs is due to agricultural activity. A significant portion (10% or more) may be attributed to combustion sources derived from combustion of fossil fuels. A simple mixing box model was employed in the study of particulate deposition. From this model, a value of 0.6 cm/sec for the deposition velocity of the phosphorus-containing particles was obtained. This value can now be used to test more sophisticated models.

From the work reported here, several recommendations can be made. While they are suggestions as to how the present study could have been improved, they should be applied to future studies as well. Shipboard collection of samples for atmospheric studies was found to be expensive and inefficient. Contamination from the ship and its exhaust hampered aerosol collection, and "bad" weather forced the ship to remain in port when wet deposition was occurring. In its place, a permanently anchored platform with a source of electric power should be established and adequate protection taken against contamination. In the long run, this should result in a more favorable cost-to-benefit ratio. Any attempt to determine annual inputs must cover at least two consecutive 12-month periods. The vertical distribution of aerosol concentration must be determined in order to properly evaluate the mixing box model. This was attempted in the present study but was unsuccessful. The next study should include the determination of this parameter. The validity of total fallout measurements has already been questioned. In the future, the independent

measurement of wet and dry deposition should be employed. In addition to providing more realistic input data, this will permit evaluation of the impact of any input through analysis of the chemical form of the species. Perhaps most important, a standard set of definitions should be established to classify the effective form of each species according to potential availability--for example, the soluble, reactive and total phosphorus determined in the present study.

In summary, the input of phosphorus to Lake Huron from the atmosphere has been shown to be significant. The amount entering through dry deposition has been shown to be larger than previously anticipated. For other elements (e.g. selenium and lead) this may be the predominant input mode. For this reason, additional research is needed on the long-range transport and deposition of particulate matter. Such work should be expanded to consider a large number of elements and classes of compounds whose potential impact on the lake must be known.

SECTION 3

PROCEDURES AND METHODS

EQUIPMENT

Gelman Air Sampling Kits (Bendix Environmental Science Division, 1400 Taylor Ave., Baltimore, MD; catalog No. 25001) were modified for field use by removal of the external flowmeter, attachment of locks and chains and the installation of timing devices. Several flowmeters were calibrated as a function of vacuum pressure against an absolutely (gravimetrically) calibrated wet test meter. Before and after each sample was obtained, flow rate and pressure values were recorded and the actual flow rate determined from the calibration curve for the flowmeter used. The Gelman pumps were used to collect aerosol samples on 47-mm glass fiber filters (Gelman Instrument Co., 660 S. Wagner St., Ann Arbor, MI) for nutrient analysis and on 25-mm Whatman 41 filters (Reeve Angel, 9 Bridewell Place, Clifton, NJ) for later analysis for trace metals. A vacuum increase of 5-10 cm of mercury was usually observed after sampling at approximately 42 lpm for 8 hr due to buildup on the filter. Filter holders were placed inside downward-facing plastic rain shields to prevent contamination of the samples by precipitation.

The Gelman pumps were also used to draw air through downward-facing Andersen cascade impactors (Andersen 1966). Discs of 4-mil Durethane® plastic were cut from sheets with a stainless steel cutter and were placed on stainless steel backup plates in the impactor. A Whatman 41 backup filter in an in-line filter holder was attached to the end of the impactor. A flow rate of approximately 28 lpm was used, and samples were collected for 24-hr periods. The principle of cascade impactors has been well reviewed (Lee and Goranson 1972; Andersen 1966) and will not be discussed.

High volume air samplers (General Metal Works, 8368 Bridgetown Rd., Cleves, OH) were used to collect aerosol particles on 8" x 10" glass fiber mats. The mats were weighed to constant weight before and after collecting a sample to determine the total weight gained through aspiration of a known volume of air. From this, the total concentrations of particulate matter in the air were determined. These samplers were run at 1416 lpm for 8-12 and sometimes 24-hr periods. Sections of the filter mat were also cut with a 47-mm diameter stainless steel cutter and chemically analyzed for phosphorus content.

Integrated fallout collectors were placed at each station for the period between aerosol sample collection, generally 24-30 days. These collectors consisted of a 1-gal Nalgene® bottle with the bottom one inch cut off, inverted and attached to an upright 1-gal bottle. A polyethylene sleeve was placed around the contact and secured with fiber-reinforced tape. A 17.5

mesh nylon screen was placed over the opening to reduce contamination from large objects (leaves, insects, etc.). Immediately prior to placement, 50 ml of pH=2 sulfuric acid was added to the container as a biocide and preservative. The unit was then placed in a wood-and-metal holder and hoisted to the top of a 5-m mast.

Event rain samples were collected in 0.4-m^2 rain buckets lined with polyethylene bags. The buckets were placed out when rain was anticipated and removed as soon after the event as possible (usually less than 8 hr). If the total volume collected exceeded 500 ml, the contents of the bag were agitated to mix the sample and a portion transferred to a polyethylene bottle. No attempt was made to determine the volume collected.

SAMPLING

The research vessel ROGER B. SIMONS was scheduled to anchor on station in Lake Huron for one 24-hr period each month from April through October 1975. While on station only one generator was run, to reduce the possibility of contamination. During this period, one 24-hr HiVol sample, two simultaneous 24-hr Andersen samples (one for future trace metal analysis, one for analysis for phosphorus) and three consecutive pairs of 8-hr Gelman samples (one set on Whatman 41 for metal analysis, the other set on glass fiber for phosphate) were collected. Samplers were located on the ship as shown in Figure 1.

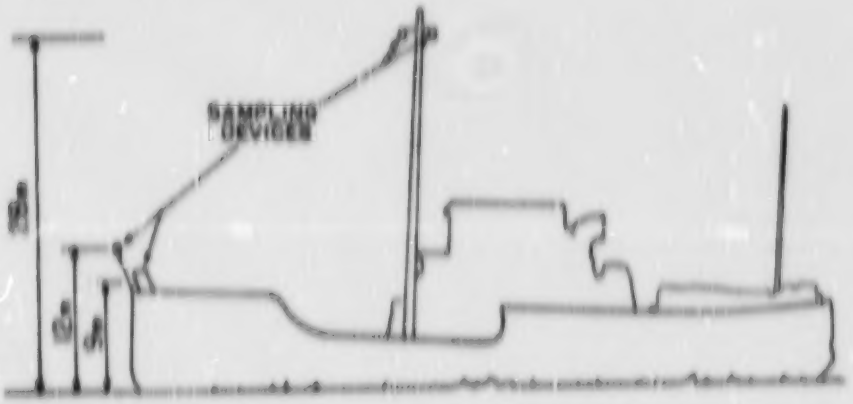


Figure 1. Location of sampling devices aboard the ROGER B. SIMONS. Gelman filter samples were collected from the mast, a HiVol sampler was located on the low deck, and Andersen impactors were elevated on a short mast at the bow. The ship was bow-anchored with aft-pointing stacks.

The 5-day land sampling period each month was coordinated so that there was at least one full day of aerosol sampling prior to and following the collection of samples from the SIMONS. Eleven sites were selected, five on the Michigan shore, six on the Canadian. The stations, located at approximately 32-km intervals, are listed in the appendix and shown on the map in Figure 3. Each site selected had the best combination of the following requirements: a source of electric power, proximity to the lake shore, remoteness from potential local sources (especially fuel-oil heated homes and agricultural land) and minimum chance of vandalism. A 5-m mast was erected at each site, and samplers were raised to the top of the mast by means of a rope-and-pulley assembly.

The 11 land stations collected two sets of samples, one for trace metal analysis, the other for phosphorus determination. On the odd numbered sampling periods, phosphorus samples were collected at Lakeport, Sanilac County Park #1 and Lighthouse County Park, Mich., and at Ipperwash Provincial Park, Bayfield and Point Clark, Ont. The other stations, Sanilac County Park #2 and Wagner County Park in Michigan and St. Joseph, Point Farms Provincial Park and Inverhuron Provincial Park in Ontario, collected samples for future trace metal analysis. During the remaining periods, the opposite sample was collected at each station, producing an oscillating grid of samples for each type of analysis. The samplers were run for 8-hr periods followed by a 4-hr down-time during which flow rate and vacuum pressure were recorded and new filters installed. The pumps were activated by a timing device to run from 1000 to 1800 hr and from 2200 to 0600 hr the following day. In the 5-day sampling period, seven samples were collected from each station. Part of the first day was used assembling the stations and most of the last day was spent dismantling the aerosol equipment and placing up the integrated fallout collectors.

A high volume sampler placed at Lighthouse County Park collected consecutive 12-hr samples during the sampling period. An Andersen impactor was operated at the Point Farms Provincial Park station for back-to-back 24-hr periods.

Exposed glass fiber and Whatman 41 filters were transferred to labelled 50 x 12 mm plastic disposable petri dishes which were then sealed in plastic bags. Andersen discs were transferred to labelled 100 x 10 mm plastic petri dishes and also sealed in plastic bags. High volume samples, previously weighed to constant weight, were wrapped in plastic, placed in a plastic bag and put into a labelled manila envelope. All samples were handled with Teflon®-coated forceps to avoid contamination.

SAMPLE PREPARATION AND CHEMICAL ANALYSIS

Phosphorus was measured as orthophosphate using a molybdenum-antimony-ascorbate procedure (Murphy and Riley 1962). This standard heteropoly acid method was automated with a Technicon® AutoAnalyser (II). A volume of approximately 1.6 ml was analysed for each sample. Blank solutions and standards containing pH=2 sulfuric acid were run during the analysis of the water and acid filter extracts, event rains and integrated fallout samples. The

Figure 2. Location of sampling and meteorological stations. Two-letter codes designate sampling stations on the Lake Huron shore and three-letter codes indicate weather stations.

persulfate digestion procedure was a modification of the method of Menzel and Corwin (1965), and digestion blanks and standards were analyzed with the digested samples.

Prior to use, all glassware was soaked in 10% sulfuric acid for a minimum of 2 hr and multiply rinsed with distilled water. Singly distilled water was used in the preparation of all reagents, for extraction of the filters and dilution of samples. The concentration of phosphorus in the water was routinely monitored. For extraction, a glass fiber filter was placed in a 60-ml suction flask. Ten 2-ml volumes of distilled water were aspirated through the filter under slightly negative pressure. The filtrate was quantitatively transferred to a 25-ml volumetric flask containing 2 drops of concentrated sulfuric acid and diluted to volume with distilled water. The extraction was then repeated using ten 2-ml aliquots of pH=2 sulfuric acid. This filtrate was transferred to a 25-ml volumetric flask (no acid present) and diluted to volume with pH=2 solution. Approximately 10 ml of each of these extracts were transferred to 16 x 150 mm Pyrex® test tubes for trans-

portation and storage. At least three unexposed filters were treated as above each month to serve as blanks.

A stainless steel cutter was used to cut 37-mm diameter discs from the previously weighed high volume mats, and duplicate discs from each filter were treated as above. Unexposed high volume mats were similarly treated to determine blank values.

Persulfate/acid digestions were performed on various samples to determine total phosphorus concentrations. A filter was placed in a 250-ml beaker, 10 ml of distilled water and 10 drops of concentrated sulfuric acid added and the sample heated to approximately 80°C. Five ml of 5% ammonium persulfate were added and the sample evaporated to dense white fumes (almost to dryness). The sample was allowed to cool, 20 ml of distilled water added, filtered through a fine porosity sintered glass funnel and diluted to 25 ml in a volumetric flask.

Monthly integrated rain samples were acidified during collection and therefore water soluble phosphorus values were not obtained. After measurement of the total volume collected, the samples were filtered through glass fiber filters to obtain total available phosphorus values; portions were filtered through pre-soaked 0.4 μm Millipore filters to determine total dissolved phosphorus, and 25.0 ml of the original sample were digested to determine total phosphorus content.

Event rains were analysed "as is" without filtration or acidification. It was later realised that for the sake of comparison, the rain samples should have been acidified to determine whether additional (but not water soluble) phosphorus would be available for uptake.

METEOROLOGICAL DATA

Meteorological data were supplied by the National Weather Service Forecast Office at Detroit Metropolitan Airport, Detroit, Mich. Teletype outputs of the Service A reports, consisting of hourly observations of temperature, dew point, wind speed, wind direction, precipitation, and cloud cover, were provided for all Michigan and Ontario weather stations.

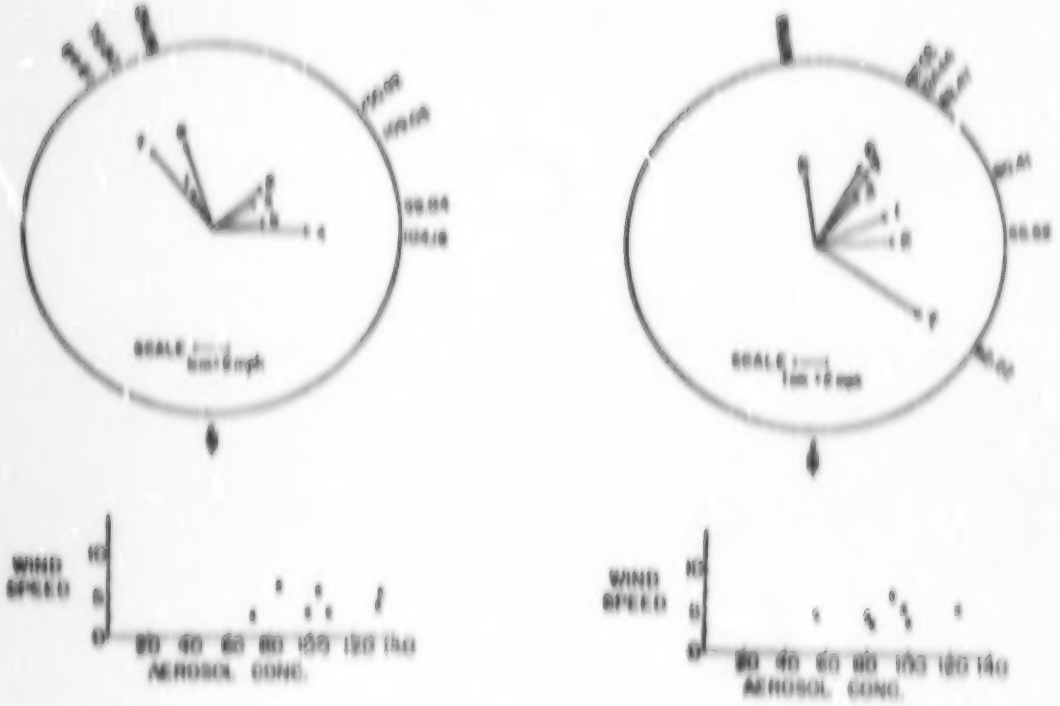
Using these data, resultant wind speed and direction vectors were calculated for the 6 hr preceding and the 9 hr of sampling for each of 12 meteorological stations, shown in Figure 2. Although some of the stations were removed from the shores of southern Lake Huron, the overall wind speeds and directions were used to provide an indication of the flow of large air masses in the southern Lake Huron basin. Meteorological data were also obtained on the SIMONS when it was stationed on the lake for sampling. Of the 13 periods where such data were available, comparison of the direction of the average 12-hr vector for all stations with the direction observed on the SIMONS (Table 1) showed that only once did they differ by more than 90° (in that one case they were 153° apart, however). Discounting this set, the average difference at 90% confidence was 43 ± 16° (n = 12). A composite wind speed and

TABLE 1: COMPARISON OF R/V ROGER R. SIMONS AND NATIONAL WEATHER SERVICE DATA ON WIND DIRECTION

Date 1975	Wind speed, km/hr		Wind direction, DEG		
	RS	NWS	RS	NWS	ΔAngle*
4/16	3.5	9.6	226	237	47
4/16-17	3.5	4.8	130	263	87
4/17	3.5	9.0	126	160	34
5/13	9.3	8.0	135	267	68
5/13-14	7.8	6.4	143	221	78
5/14	3.8	9.1	186	214	28
6/12	20.9	16.1	230	217	13
6/12-13	18.4	13.8	230	218	12
7/09-10	6.2	12.2	208	292	88
7/10	12.8	6.9	(128)	280	152
7/16	15.2	9.4	201	200	1
7/16-17	13.5	5.3	208	191	17
7/17	5.4	4.6	237	203	34

*Eliminating highest value, 90% confidence limit is 42° ± 16.0° variation (n = 12); and using all values, the value is 51° ± 21.9° variation (n = 13).

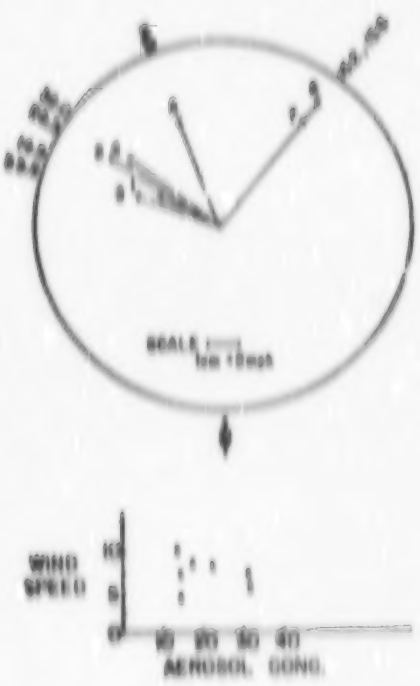
direction vector was obtained for the 12-hr period (interval of sampling) by taking the average wind speed and direction from all stations. This vector is shown for each sampling period in Figures 3a through 3g.



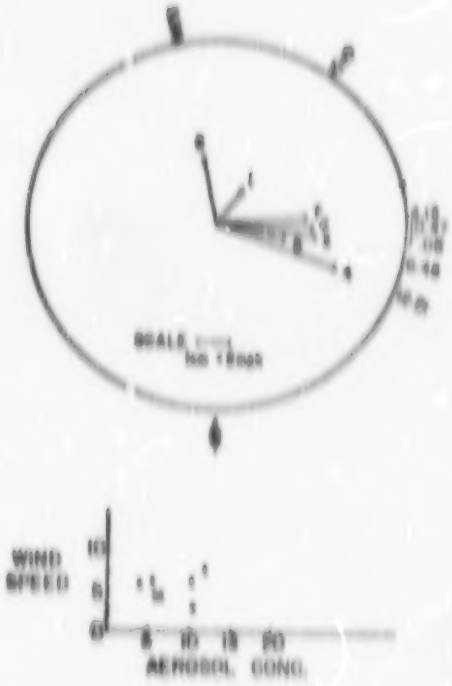
(a) April sampling period.

(b) May sampling period.

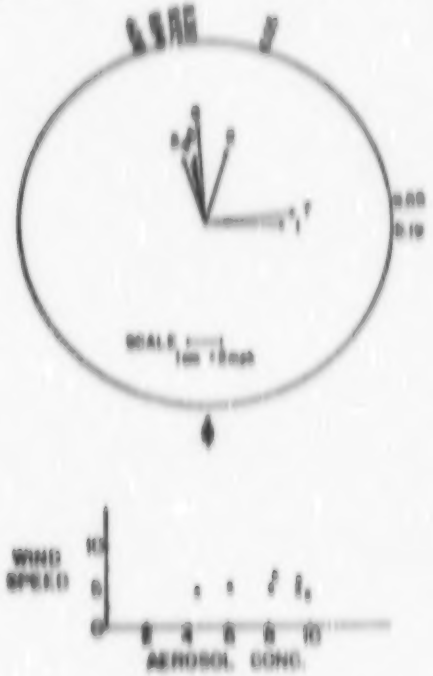
Figure 3. Wind speed, direction, and aerosol concentration roses. Arrows indicate wind direction; concentration of total available phosphorus measured during that period is indicated at the perimeter of the circle. The lack of correlation between total available phosphorus concentration and wind speed is shown below each wind rose.



(c) June sampling period.



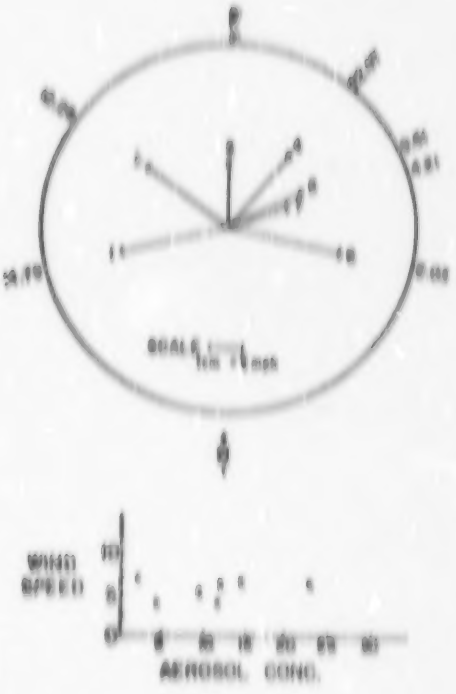
(d) July sampling period.



(e) August sampling period.

Figure 3 continued.

(f) September sampling period.



(g) October sampling period.

Figure 3 continued.

SECTION 4

RESULTS AND DISCUSSION

TOTAL FALLOUT

The integrated fallout samples provided a means for determining the total input of phosphorus. They contained both wet and dry deposition which had occurred over a fixed area at a particular point during a given period. Analysis of the phosphorus content of these shore-based samples provided an upper-limit estimate of the phosphorus input to the lake surface from the atmosphere. In determining these inputs, the mean value of the 11 stations at a 90% confidence limit was used. The 90% confidence limit was selected as the indicator of statistical reliability and will be indicated whenever possible.

Since the samplers contained sulfuric acid as a preservative and biocide, the water soluble portion of the phosphorus in the sample was not determined; however, total available phosphorus was determined on aliquots of the acidified sample after filtration through glass-fiber and/or Millipore filters to remove suspended particulate matter. The efficiency of this filtration was verified by digestion of part of the filtrate and subsequent comparison of the phosphorus content of the digested and undigested filtrate, which showed that no additional phosphorus was present in the digested sample. Due to complications in the digesting procedure, total phosphorus values were obtained only for August-December integrated samples. Comparison of available and total phosphorus in the integrated samples indicated that 32 ± 10% (n = 24) of the total phosphorus in these late fall samples was present as available.

The volume and available phosphorus concentration of each sample is listed in Table 2. To correct for potential volume losses, the amount of available phosphorus (volume x concentration) was calculated for each sample and the mean monthly value at 90% confidence used to determine the deposition rate for each sampling period, as discussed below.

Average phosphorus contents of the samples were plotted (Fig. 4) to illustrate the seasonal variation of total available phosphorus input from the atmosphere. This input peaked in the late spring and rose again in the early fall in a pattern that roughly corresponds to agricultural activity in the Lake Huron basin. The May-June samples also showed marked evidence of biological activity despite the screen and biocide. Most of the samples for this period were dark green or yellow, and microscopic examination showed algal growth, pollen, and even small insect larvae. A significant amount of the phosphorus input during this period was therefore associated with biological activity.

TABLE 2. INTEGRATED PELLET SAMPLES—VOLUME COLLECTED (ml) AND AVAILABLE PHOSPHORUS CONTENT (ppb), 1975

Station code	4/28–5/22		5/25–6/9		6/23–7/7		7/11–8/4		8/12–9/15		9/29–10/6	
	Vol	[P]	Vol	[P]	Vol	[P]	Vol	[P]	Vol	[P]	Vol	[P]
LT	710	15.78	—	—	670	10.22	1360	1.79	730	2.81	425	3.25
MC	480	12.66	1810	200.60	175	124.51	460	5.33	1135	110.2	208	122.7
SL	185	68.08	1820	54.26	325	9.03	780	31.22	1215	0.44	—	—
SE	1190	5.42	2516	22.36	175	124.55	1850	1.76	900	110.7	200	2.60
DP	595	4.18	995	37.67	610	124.99	2527	2.17	—	—	250	120.3
DY	2415	1.24	1160	8.22	—	—	1180	4.05	740	21.0	345	77.8
SU	1140	7.71	2130	5.99	170	124.57	260	26.98	130	111.1	320	16.4
BK	1115	2.23	885	3.73	620	4.74	1140	2.74	450	1.24	215	0.50
PF	970	41.87	530	28.83	960	7.11	—	—	1105	17.9	200	2.00
PC	365	35.49	480	69.53	475	124.66	360	—	3180	47.7	90	1.55
IN	215	22.26	410	736.3	300	3.94	190	16.94	2560	0.9	430	1.21
	847	33.3	1273	116.1	418	64.9	931	10.5	1215	42.8	268	35.1

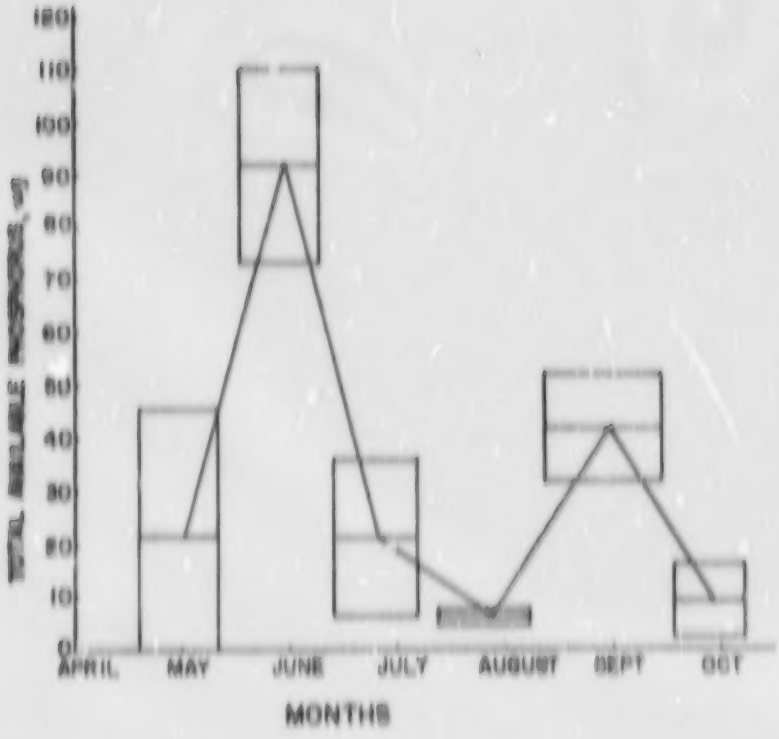


Figure 4. Monthly variation of available phosphorus in integrated fallout samples. The brass indicate the 90% confidence limits for each monthly sample set.

To determine whether the samplers were sampling the actual amount of precipitation which fell during the sampling period, the volume collected was converted to an average rainfall in inches. This number was compared to the amount of precipitation recorded at four weather service stations on the Michigan shore of Lake Huron. As shown in Table 3, the correlation was good in the spring but deteriorated during the hotter months due to evaporation losses. The input of available phosphorus from the atmosphere was expected to follow the amount of rainfall for each period. Comparison of the total available phosphorus content of the integrated fallout samples with the actual rainfall reported by the U.S. Weather Service for that period (Fig. 5) showed that this was not the case, however. This was substantiated by the seasonal variation in the phosphorus content of event rain samples.

WET DEPOSITION

Event rain samples were collected during each sampling trip to determine the phosphorus content of rain. Comparison of remote and urban samples showed

TABLE 3. COMPARISON OF OBSERVED AND CALCULATED RAINFALL

Sampling period	Calculated* rainfall, cm	Observed** rainfall, cm	% calc/obs
4/18-5/12/75	5.21	5.49	95.
5/16-6/9	7.59	8.03	95.
6/13-7/7	2.49	5.18	48.
7/11-8/8	5.56	8.33	67.
8/12-9/15	7.24	8.41	86.
9/19-10/6	1.60	3.35	48.

*Rainfall, in = $\frac{\text{average volume, cm}^3}{\text{collector area, cm}^2}$ =

$$\frac{\text{volume}}{167.5\ \text{cm}^2}$$

**Average of Weather Service data from Saginaw, Beaverton, Harbor Beach and Sandusky, Mich., weather stations.

the effect of industrial inputs of phosphorus to the atmosphere. During June, event rain samples were taken on the SIMONS which was docked approximately 5 km downstream from the mouth of the St. Clair River in an area of industrial development. The mean value for total soluble phosphorus for five samples collected at the remote stations during this period was 7.1 ppb; in the Port Huron/Sarnia sample it was 15.7 ppb. In October, a value of 1.96 ppb was observed in the remote samples (3) whereas a sample taken at North Street, a suburb of Port Huron, contained 36.6 ppb of soluble phosphorus.

Analysis of the event rain samples collected provided a means of determining the contribution of wet deposition to the total atmospheric phosphorus input to the lake. No rain events occurred during the sampling periods in April or May. The data for the remaining months, shown in Figure 5 and Table 4, indicated that a definite seasonal trend existed which was not that of the total fallout samples. The mean value of total soluble phosphorus, in parts-per-billion, 90% confidence limit and number of samples collected for the months of June through October are: 7.09 ± 3.05, (5); 8.65, (1); 4.89 ± 3.65, (4); 0.99 ± 0.13, (4); and 1.96 ± 4.00, (3), respectively. Although these values represent only the soluble fraction of the available phosphorus, it is still possible to estimate the contribution of precipitation to the integrated fallout samples. This value would be a lower limit, and the actual contribution is expected to be approximately double this value (Murphy 1974).

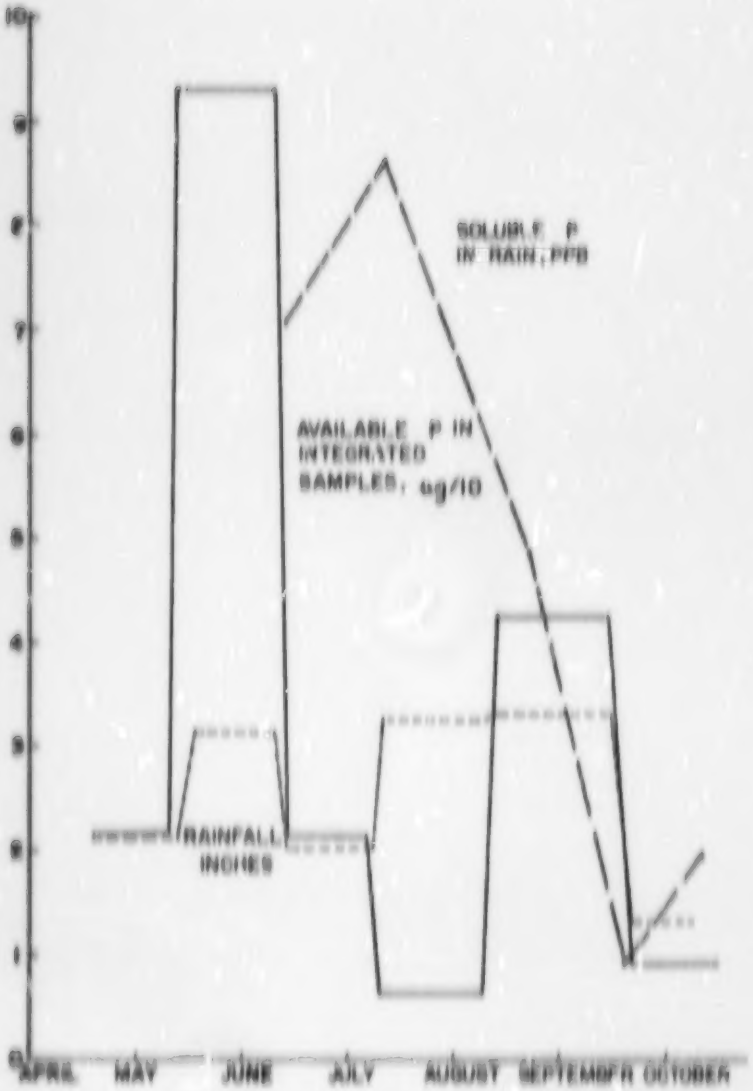


Figure 5. Comparison of rainfall, concentration of reactive phosphorus in rain and total available phosphorus collected in integrated samples, April-October 1975. Units for the scale are indicated on the figure.

TABLE 4. PHOSPHORUS CONTENT OF EVENT RAIN SAMPLES, JUNE-OCTOBER 1975

Station code	Date	Time	[P] ppb	[P] Average
LN	6/11	?	6.51	
IN	6/12	1000-1800	12.19	
IN	6/12-13	1800-1000	4.31	7.09
LP	6/11	?	4.92	± 3.05
RS	6/12	1750-1815	3.99	
PS	6/12-13	2300-0800	7.86	
PH	6/11-12	2000-0000	15.69	15.69
IN	7/10	0910-1730	8.65	8.65
PH	7/10	0830-0930	11.03	11.03
LP	8/20-21	2000-0808	7.72	
LP	8/21	0810-2030	7.25	4.89
IN	8/20-21	1800-1800	1.28	± 3.65
BJ	8/21	0715-2045	4.32	
LT	9/13	1230-1814	1.01	
LT	9/18-19	1814-0600	0.27	0.95
IN	9/18	1330-1745	0.95	± 0.13
IW	9/18	?	1.03	
IW	10/8-9	2300-2100	0.26	1.96
IN	10/9	1400-1730	0.95	± 4.00
LP	10/8-9	1945-0620	4.67	
NS	10/8	1345-2200	36.57	36.57

TOTAL AEROSOL LOADING

HiVol samples were collected at the Lighthouse County Park station near Huron City, Mich.; and on board the SIMONS. Starting in June, these samples were used to determine the total particulate concentration in the air (total loading) by weighing the filter mats to constant weight before and after sampling. The values for total loading in ug/m^3 are listed in Table 5 with station and monthly averages. These average values have been plotted against month (Fig. 6) to indicate the seasonal variation of total loading. As with the integrated fallout samples, September showed an elevated load of particulate matter in the air. Unfortunately, no data were available for the spring months.

These total loadings have been used to determine whether a particulate concentration gradient exists across the lake. If the deposition of particu-

TABLE 5. HIVOL LOADINGS, JUNE-OCTOBER 1975

Sta	Date	$\mu g/m^3$	Station avg.	Monthly avg.
LT	6/8-10	18.4		
LT	6/10-11	25.8		
LT	6/11-12	19.7	25.7	
LT	6/12-13	39.0		24.2 ± 5.4
WRS	6/12	19.1		
WRS	6/12-13	27.3	22.2	
WRS	6/13	20.3		
LT	7/7-8	51.3		
LT	7/8	11.8		
LT	7/8-9	9.8		
LT	7/9	19.7		
LT	7/9-10	7.2	18.9	
LT	7/10	5.1		14.1 ± 9.9
LT	7/10-11	7.6		
RS	7/9	11.4		
RS	7/9-10	1.1	6.27	
LT	8/18-19	8.8		
LT	8/19	6.8		
LT	8/20	11.25		
LT	8/20-21	---	11.60	11.6 ± 4.0
LT	8/21	17.6		
LT	8/21-22	13.7		
PH	8/22	23.9	23.	
LT	9/14-15	36.7		
LT	9/15-16	69.5		
LT	9/16	50.1		
LT	9/16-17	73.1		
LT	9/17	64.7	51.0	
LT	9/17-18	49.9		53.7 ± 8.1
LT	9/18	39.9		
LT	9/18-19	24.1		
RS	9/15	53.9		
RS	9/15-16	61.8	57.9	
RS	9/16	56.0		
LT	10/8-9	31.0		
LT	10/9	12.7		
LT	10/9-10	45.2		
LT	10/10	62.4	33.5	33.9 ± 19.1
LT	10/10-11	12.9		
LT	10/11			
LT	10/11-12	16.9		

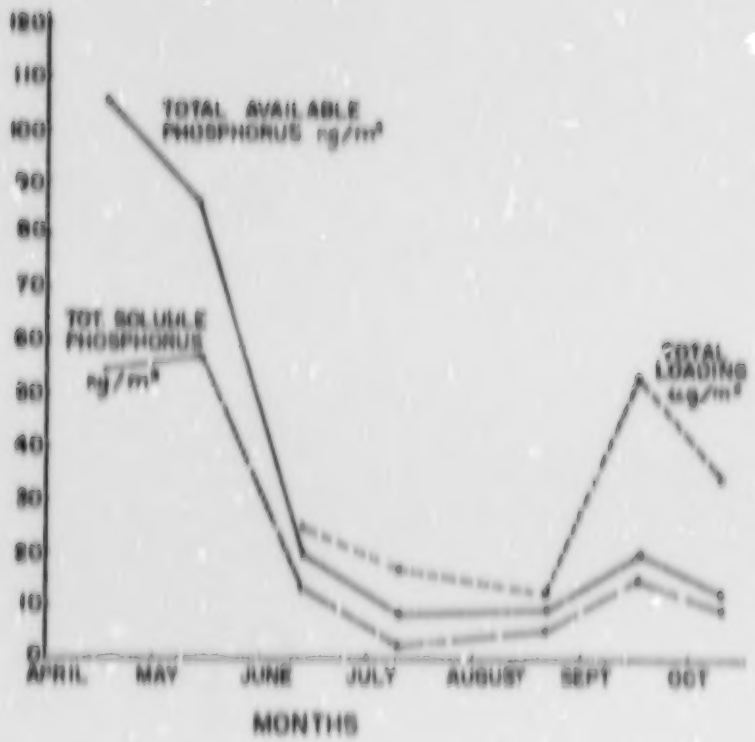


Figure 6. Relationship between total aerosol concentration, soluble and available phosphorus.

late matter is sufficiently rapid, the concentration of particulate matter over the lake should be less than that in the air over the upwind shore. Although the number of samples was small and the locations of the samplers different, it appears that such a gradient does exist. The June samples were collected during a period when the wind was from the southwest (~218°). The small difference between land and lake samples was due to the proximity to the Michigan shore of the SIMONS, which was anchored 5 km from the shore due to bad weather. Nevertheless, the values obtained from the SIMONS were lower than the land-based samples (27.3 vs. 39.0 $\mu g/m^3$). In July, the SIMONS was on station at mid-lake and was again downwind from the Michigan shore. Aerosol concentrations for 9 July were 19.7 and 11.4 $\mu g/m^3$ for the land and lake samples, respectively. During the following period a strong rain occurred, reducing the total aerosol concentration. Again the value from the Michigan shore (7.2 $\mu g/m^3$) was higher than that at mid-lake (1.1 $\mu g/m^3$). In September, however, total aerosol loadings were slightly higher in samples taken from the SIMONS (52.2 $\mu g/m^3$) relative to the land-based samples (37.2 $\mu g/m^3$). During this period, the wind was from the south (191-203°) and had little cross-lake direction so a comparison was not possible.

AIRCRAFT SAMPLING

During the week of 15-19 September, the Environmental Protection Agency, Las Vegas, Nev., provided an aircraft for use in the study. The aircraft, a B-26, was equipped with a DME, Bendix ozone, TECO nitric oxide, temperature, dewpoint, nephelometer, altitude and Dasibi ozone monitors and a particulate sampling system. The aircraft was used to determine the mixing layer height from nephelometer data taken during spirals, to collect particulate samples at three heights to determine the altitude profile of aerosol particles, and to track a given parcel of air by sampling particulate matter at various points along the wind trajectory at a given height. Flight paths are depicted on a map of southern Lake Huron in Figure 7. Data records for the nephelometer were produced every 5 sec. A summary of the particulate samples collected is given in Table 6.

The first sampling mission was flown 15 September (Fig. 7a). The aircraft rendezvoused with the SIMONS at 1312 hr. A spiral from 2743 m to 244 m MSL at a descent rate of 2.54 m/sec was performed over the ship. A 93 km/hr crosswind pattern at 670 m MSL was then begun at 1334:20 using the ship as the center point. The wind was reported by the Weather Service to be from 240°. Wind streaks on the lake surface seemed to confirm this. Wind speed was estimated from aircraft drift to be about 56 km/hr. Filter No. 1 ran from first rendezvous with the ship to the end of the first crosswind pattern. This filter includes the spiral and the crosswind pattern.

At the end of the first crosswind pattern, a second spiral was performed over the ship from 2743 m to 244 m MSL. Filter No. 2 was run during the second spiral. Assuming a 56 km/hr wind, the air parcel sampled during the first crosswind pattern was calculated to have moved approximately 46 km east of the first pattern. The second crosswind pattern was then flown parallel to the first but 46 km downwind. Filter No. 3 was run during all of pattern two. A third and final spiral was performed over the ship from 2743 m to 244 m MSL before returning to Selfridge Air National Guard Station to refuel and recalibrate.

Weather conditions prevented sampling missions on all but Monday and Wednesday. Mission One on Wednesday, 17 September (Fig. 7b), attempted to measure the altitude profile of phosphate concentrations. A box pattern with sides of approximately 64 km was flown over the lake at three altitudes, collecting a filter sample at each altitude. Although a light wind was blowing from the east during this mission, the box pattern should block out the effects of pollutant transport. Filters were collected at 610 m, 488 m, and 166 m MSL. The lake surface is approximately 180 m MSL.

Mission Two on 17 September (Fig. 7c) attempted to measure the effect of particle transport and fallout over the lake. Unfortunately, the wind was not blowing by then, and the air pump failed near the beginning of the second filter. The first filter ran during two passes between Grand Bend and Point Clark, Ont., for 59 min at 488 m MSL. The second filter ran for only 2.25 min, from a point near Lexington, Mich., to a point about 13 km north of Lexington. If the wind had been blowing, the second crosswind pattern would

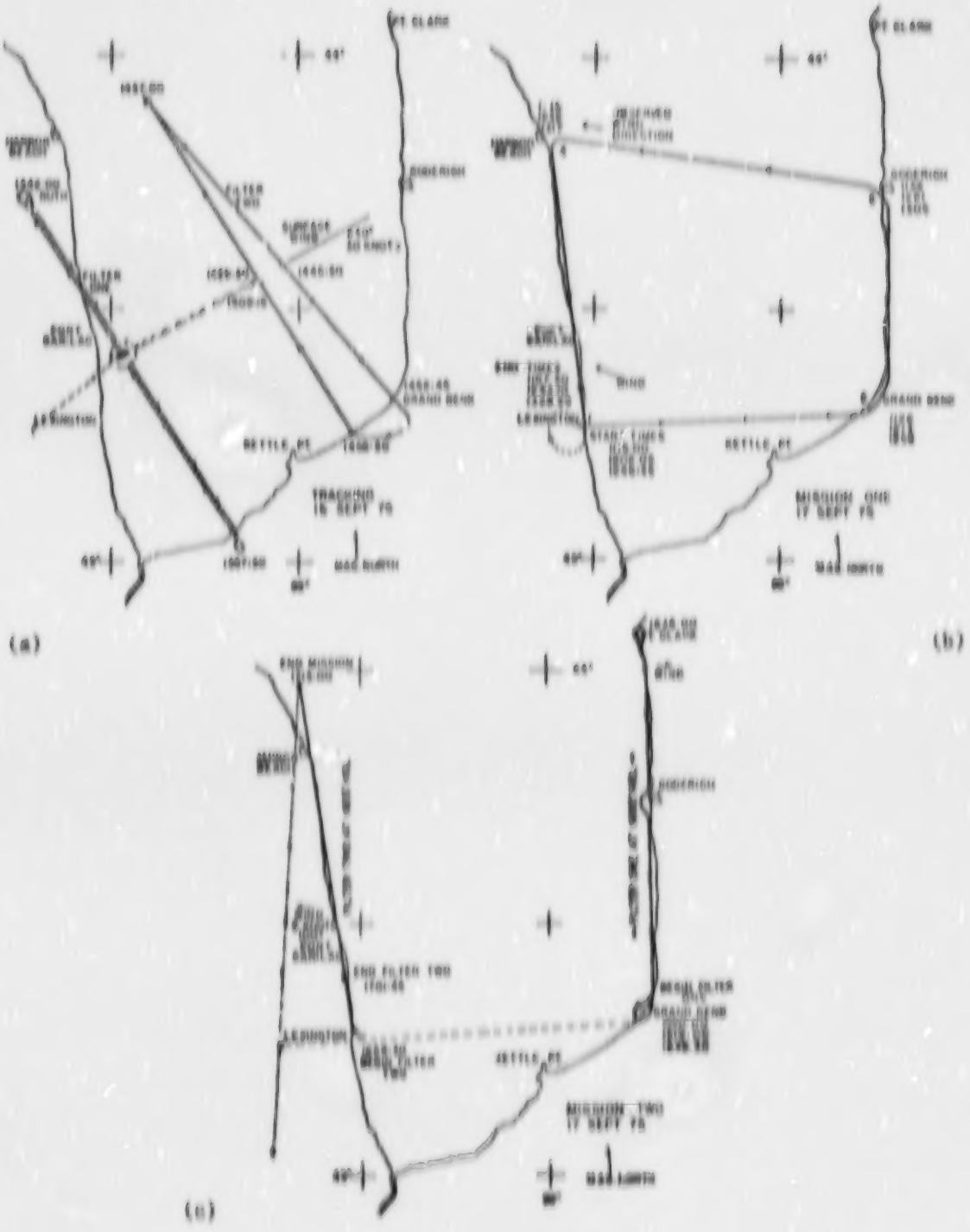


Figure 7. Flight paths for aircraft sampling, 15-17 September 1975.

TABLE 6. AIRCRAFT PARTICULATE SAMPLE SUMMARY

Date	Sampling time	Vol. m^3	Tot. vol. P, ng/m^3	Tot. recov. P, ng/m^3	Tot. bound P, ng/m^3	Tot. P ng/m^3	% Accil. total P	Remarks
9/25/75	1551-59-1602-07	3.54	1.58	21.45	1.54	25.42	86.9	Includes first spiral plus first crosswind pattern
	1609-07-1615-15	1.81	2.20	2.67	7.54	10.53	27.4	Second spiral only
	1619-23-1625-32	1.85	1.64	4.32	6.31	12.07	48.6	Second crosswind pattern
9/29/75	1111-05-1158-08	2.74	7.38	5.38	7.39	18.17	62.4	Box pattern at 610 x 975.
	1202-09-1242-10	2.56	8.47	5.84	7.08	21.39	66.9	Box pattern at 488 x 975.
	1247-09-1253-08	2.58	8.81	—	7.77	17.45	>56.1	Box pattern at 366 x 975.
	1333-08-1349-18	2.91	1.38	5.84	2.45	9.17	77.6	Along Canadian shoreline at 488 x 975.
	1409-39-1701-45	8.13	6.55	8.38	2.37	17.48	87.8	Along U.S. shoreline at 488 x 975.

have been performed at a distance downwind from the first pattern according to the estimated transport speed. The decision to sample along the western shoreline was made after it was apparent that the wind was too light to measure transport effects.

Figure 8 shows the nephelometric data from the three spirals plotted against height. From these data, the mean height of the mixing layer is approximately 1200 m above the lake surface. This value agrees with that of 1200-1300 m obtained from rawinsonde data by Portelli (In press) for the mean afternoon maximum mixing heights in summer over the southern portion of Canada, including the Great Lakes. This value of 1200 m will be used in the calculation deposition velocities discussed below.

In this study, eight filter samples were collected. The first attempt at obtaining a horizontal gradient was confused by the inclusion of spirals while the filter samples were being collected; thus the fixed altitude requirement was not met. Mission Two of the 17 September sampling failed to establish a horizontal gradient since no sample was collected at a second point and since the wind speed was almost zero. Thus the altitude profile samples taken on 17 September were the only "good" samples. Unfortunately these did not include a sample above the mixing height for comparison. Intervals of 122 m also appear to be too small to establish a significant gradient. Values for all filter samples were higher than land-based and shipboard samples by a factor of about 4, averaging somewhere near 160 ng/m^3 using the volume data supplied by NERC. The only explanations for this exceedingly high difference are that either the samples were contaminated from the aircraft (or during handling) or that the reported volume aspirated is wrong. The latter is supported by the agreement between aircraft and land-based samples for percent soluble and available phosphorus. In either case, the particulate samples cannot be considered valid. It should be noted, however, that the feasibility of the use of an aircraft as a workable platform for particulate sampling has been established. The continued investigation of height profiles is necessary, and this work has established criteria for such future work.

AEROSOL SAMPLES

To determine the availability of phosphorus to the lake, airborne particulate samples were analyzed for three fractions--water soluble, acid (pH=2) soluble, and bound phosphorus. Results of the analysis of samples collected in September are shown in Table 7. Of the total phosphorus in the aerosol, 28.7% is immediately available to the biomass, 48.2% of the aerosol phosphorus is potentially available for use in the short term, and over half of the phosphorus entering the lake from dry deposition is not soluble in either water or pH=2 sulfuric acid. This fraction must be present as either inorganic salts (insoluble metal phosphates) or as organically bound phosphorus. While this phosphorus is not immediately available and probably settles to the bottom, it may eventually be released to the lake water through some aging process at the sediment-water interface (Rannerman et al. 1975). Clearly, this fraction should be investigated further to determine its chemical and physical composition and its potential release.

Figure 4. Plots of temperature vs. altitude

TABLE 7. ANALYSIS OF AEROSOL SAMPLES FOR SOLUBLE, REACTIVE AND BOUND PHOSPHORUS CONTENT REPORTED IN ng/m³

Sample	[P] Sol	[P] React.	[P] Bound	Total P	%Sol.*	Avail.**
BJ1	17.47	10.90	33.05	51.42	28.4	46.2
BJ3	5.01	4.89	25.21	15.11	14.3	28.2
BJ7	14.53	4.14	17.90	36.57	39.8	51.1
BY2	5.10	9.79	----	----	----	----
BY4	4.00	14.73	19.93	38.66	10.3	48.4
BY6	7.29	4.71	11.66	23.69	30.8	51.6
PP1	4.10	2.63	11.78	18.51	22.2	36.4
PP3	8.37	9.82	19.25	37.44	23.4	48.6
PC6	6.36	----	16.40	26.76	23.7	----
LP3	3.33	2.23	10.60	16.18	20.7	34.3
LP5	7.95	4.23	11.12	23.30	34.1	51.3
LP7	14.06	1.90	1.73	21.69	64.8	81.8
IW2	11.1	2.05	7.48	12.86	25.9	41.8
IW4	2.99	4.34	16.02	23.35	12.8	31.4
IW6	9.58	2.58	6.57	18.73	51.1	64.9

* Avg. = 28.7 ± 7.7% at 90% confidence (n = 14).
** Avg. = 48.2 ± 7.4% at 90% confidence (n = 13).

The seasonal variation of soluble, reactive and total available phosphorus in the aerosol is shown in Table 8 and in Figures 6 and 9. Individual sample concentrations are listed by month in Table 9. The seasonal variation of the aerosol phosphorus is similar to both the integrated fallout samples (Fig. 4) and the total aerosol loading. The rise in phosphorus input from all atmospheric sources in the spring and fall was previously suggested to be due to agricultural activity. The variation in the percent soluble of available phosphorus, also listed in Table 8, tends to support this view. It may be that the addition of orthophosphate-enriched fertilizers increases the amount of water-soluble phosphorus, and the higher percentages observed in the spring and fall are due to increased aerosol injection of agricultural soil.

To determine whether any relationship existed between wind direction and aerosol phosphorus content, wind roses shown in Figure 3 were constructed. No correlation was observed between total aerosol, available phosphorus and wind speed or wind direction. Since aerosol particles can travel distances of over 300 km before deposition, meteorological data taken in the lake basin may not accurately reflect meteorological conditions at the source of the aerosol. It is likely, however, that a longer term study with more data would be able to determine the relationship between wind direction and aerosol concentration.

TABLE 8. AVERAGE MONTHLY AEROSOL PHOSPHORUS CONCENTRATION

Sampling period (1975)	Total soluble phosphorus, ng/m^3	Total reactive phosphorus, ng/m^3	Total available* phosphorus, ng/m^3	% Soluble of available
4/14-18	54.73	90.34	105.07 ± 19.0	52.1
5/12-16	56.90	29.15	86.05 ± 16.6	66.0
6/9-13	12.57	6.53	19.11 ± 3.5	65.8
7/7-11	1.83	5.76	7.59 ± 3.1	24.1
8/18-22	4.31	3.74	8.05 ± 1.9	53.5
9/15-19	13.97	5.13	19.10 ± 3.1	73.1
10/8-12	8.01	3.55	11.56 ± 2.1	69.3

*90% confidence limit.

PARTICLE SIZE DISTRIBUTION OF PHOSPHORUS

Aerosol particles can be divided into three size categories which roughly correspond to source modes. The fraction <0.1 μ has been attributed to gas phase reactions and particles formed from condensation of vapors produced in combustion processes. For example, aviation and automotive fuels contain organophosphorus additives to reduce corrosion; open-hearth furnace fumes have been found to contain 0.3% of phosphorus pentoxide. The size range 0.1-1.0 μ is generally associated with continental erosion and to a lesser extent with sea spray and the smaller fractions of fly ash. Soil has been estimated to contain in the area of 650 ppm phosphorus by weight (Bowen 1966, p. 196). Application of phosphate-enriched fertilizers increased this value considerably. The particles in the size range of 1.0-10 μ are usually derived from sea spray (not a significant contribution from the freshwater Great Lakes, however), fly ash, biological injection (spores, bacteria) and the larger fraction of continental dust. The fly ash from iron and steel production contains an average of 1.3% P_2O_5. Fly ash from oil-fired boilers has been estimated to contain 0.9% phosphorus, as P_2O_5 (Athanassiadis 1969). Puroglove (1957) has estimated that by 1980 the electric utility industry alone will produce 45 million tons of fly ash containing 400,000 tons of phosphorus pentoxide each year. The fraction of this fly ash which will enter the air is not known. Incineration of refuse would also contribute to this size fraction. Murphy (1974) concluded that the atmospheric inputs of phosphorus from the fertilizer industry, soil, and the combustion of fuel are predominant. If the size distribution of phosphorus in the aerosol is known, it is possible to estimate the general origin of the particles. Knowledge of the size distribution is also useful in evaluating the accuracy of such parameters as the residence time and hence deposition velocity.

Due to the relatively small amounts of phosphorus anticipated on each stage, the 24-hr Andersen samples were collectively digested by stage for each month. As a result, the minimum sampling time was 72 hr. Backup filters

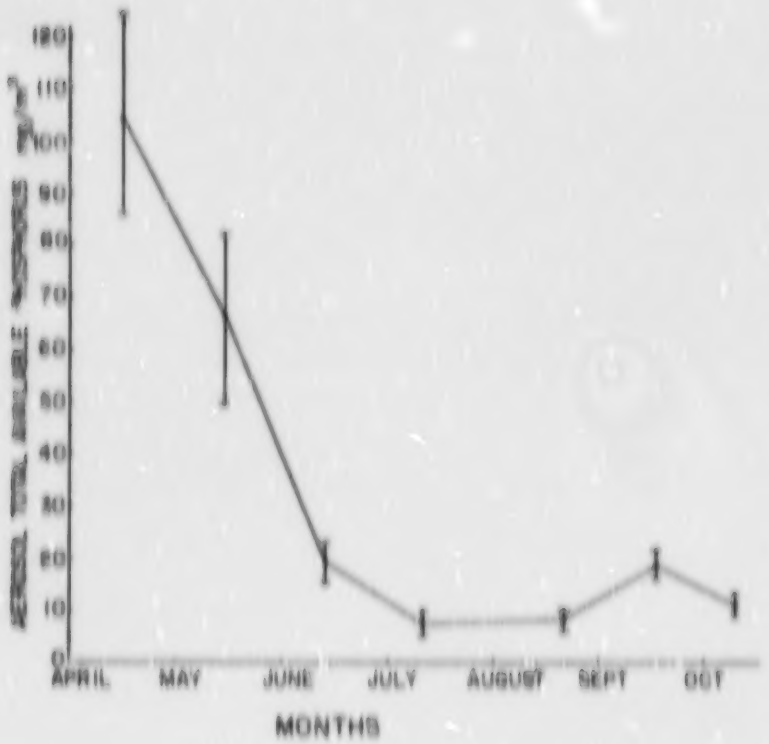


Figure 9. Monthly aerosol total available phosphorus. 90% confidence limits are indicated by the bars.

were not analyzed and therefore as particles <0.1 μ were not routinely collected. In August and September, 8-stage Andersen samples were collected which indicate that a significant (>10%) fraction of phosphorus was contained on the particle <0.1 μ. Table 10 lists the phosphorus distribution of particles <0.1 μ by size range, and the data are plotted in Figure 10. The mass median diameter is approximately 1 μ with at least 28.5% of the phosphorus found on particles less than 0.5 μ. The particle size distribution is bimodal for all months, the peak of the lower mode appearing to shift to the 0.3-0.5 μ range during May, June and July from the range of 0.5-0.9 in April, August and September. No seasonal trend can be observed from these data, however. From the mass median diameter, it appears that a significant fraction is due to continental erosion. This supports the conclusion that spring and fall rises in phosphorus content of the aerosol and total fallout samples are related to the agricultural injection of soil particles. A significant proportion (at least 10%) also originates from combustion sources.

DETERMINATION OF DEPOSITION VELOCITY

The concentration of total available phosphorus in the aerosol samples collected at each station is shown in Figure 11. It was qualitatively observed

TABLE 9. AEROSOL CONCENTRATION OF SOLUBLE AND REACTIVE PHOSPHORUS BY STATION FOR THE MONTHS APRIL–OCTOBER 1975

AEROSOL INPUT: APRIL

Filter number	Total soluble phosphorus, ng/m³	Total reactive phosphorus, ng/m³	Total available phosphorus, ng/m³
LF1	29.95	54.45	84.40
LF3	64.43	74.24	138.67
LF5	38.71	64.61	103.31
LF7	64.18	70.37	134.55
VG2	60.56	55.01	115.57
VG4	65.28	54.46	119.74
VG6	75.15	69.51	144.66
BF3	20.15	33.69	53.84
BF5	17.45	26.80	44.24
BF7	23.40	24.61	48.01
BF9	10.44	31.19	41.63
LP1	17.41	26.06	43.47
LP3	44.35	35.13	78.48
LP5	9.32	30.55	39.88
LP7	24.23	47.03	71.26
VG2	90.75	113.41	204.15
VG4	67.75	54.41	122.16
BJ1	68.71	29.69	98.40
BJ3	82.12	98.45	180.57
BJ5	177.53	93.72	271.24
BY2	103.20	88.62	191.82
BY4	157.55	93.78	251.33
BY6	100.70	62.64	163.34
PF1	58.76	26.11	84.87
PF3	56.18	114.71	170.89
PF5	54.13	29.74	83.88
PG2	77.05	24.41	101.45
PG4	107.79	41.82	149.61
PG6	70.28	26.59	96.87
IB1	18.75	34.30	53.05
IB3	15.11	20.57	31.68
IB5	18.28	33.41	51.70
RB1	12.71	30.30	43.01
RB2	3.76	23.72	32.49
RB4	9.44	23.76	33.21

TABLE 9 (continued). AEROSOL INPUT--MAY

Filter number	Total soluble phosphorus, ng/m³	Total reactive phosphorus, ng/m³	Total available phosphorus, ng/m³
LF1	9.90	25.65	35.54
LF3	33.63	57.57	91.20
LF5	91.61	136.80	208.41
LF7	164.64	53.67	218.31
WG4	17.71	80.88	98.59
WG6	135.29	60.64	195.93
BJ1	46.94	42.87	89.81
BJ3	44.60	9.38	54.88
BJ5	104.55	36.73	141.28
BJ7	89.34	6.31	95.65
BJ2	54.38	9.55	61.92
BJ4	94.44	116.36	210.80
BJ6	27.55	14.30	41.85
LP1	45.58	12.09	57.67
LP3	122.68	61.27	183.96
LP5	42.38	15.25	57.63
LP7	81.20	7.50	88.70
IW1	48.06	5.41	53.47
IW3	11.23	4.68	15.91
IW5	18.03	8.01	26.05
IW7	36.66	5.11	41.97
BJ2	51.35	41.01	92.36
BJ4	68.64	46.84	115.49
BJ6	64.66	18.12	82.78
BY1	18.47	2.95	21.42
BY5	77.46	24.41	101.86
BY7	54.10	12.11	66.21
PF2	17.99	2.67	20.66
PF4	57.12	45.40	102.52
PF6	49.24	11.95	61.19
PC3	54.52	12.88	67.40
PC5	19.45	25.25	64.70
PC7	20.87	21.58	42.45
IN1	178.27	46.29	224.56
IN2	23.23	21.92	45.15
IN4	73.81	20.98	94.79
IN6	83.64	19.68	103.31
RB1	19.76	0.16	19.94
RB2	25.45	0.16	25.61
RB3	17.34	1.89	19.23

TABLE 9 (continued). AEROSOL INPUT--JUNE

Filter number	Total soluble phosphorus, ng/m³	Total reactive phosphorus, ng/m³	Total available phosphorus, ng/m³
LV1	4.30	4.14	8.43
LV3	----	----	----
LV5	2.01	2.76	4.78
LV7	----	0.51	0.61
WG2	7.21	4.36	11.57
WG4	25.25	11.43	36.68
WG6	5.70	7.31	13.01
BL1	7.51	2.98	10.49
BL3	26.15	10.82	36.98
BL5	23.97	5.79	29.76
BL7	13.69	4.93	18.62
BJ2	23.43	3.37	26.80
BJ4	39.42	2.06	41.47
BJ6	10.13	6.21	16.53
LP1	16.92	6.28	23.20
LP3	22.68	6.95	29.63
LP5	10.37	3.95	14.31
LP7	19.41	3.17	22.60
LW1	10.46	4.50	14.96
LW3	31.50	38.02	69.52
LW5	1.91	2.26	4.17
LW7	15.66	14.13	29.79
BJ2	37.32	5.77	42.99
BJ4	28.02	5.84	33.86
BJ6	8.60	6.50	15.10
BY1	6.66	15.26	21.92
BY3	9.20	7.92	17.12
BY5	5.65	1.10	6.76
BY7	7.41	7.78	15.19
PF2	9.01	11.58	20.59
PF4	14.01	8.68	22.69
PF6	6.24	6.11	12.35
PC1	5.02	5.17	10.19
PC3	7.46	5.28	12.74
PC5	1.36	1.81	7.17
PC7	4.14	7.66	10.80
IN2	2.01	7.50	9.51
IN4	19.49	5.67	25.16
IN6	5.00	4.58	9.58
PH2	----	2.73	2.50
BS7	----	1.10	2.82

TABLE 9 (continued). AEVOSOL INPUT--JULY

Filter number	Total soluble phosphorus, ng/m³	Total reactive phosphorus, ng/m³	Total available phosphorus, ng/m³
LF1	6.03	6.15	12.18
LF3	0.04	1.18	1.22
LF5	----	1.17	1.17*
LF7	----	11.86	11.86*
WO2	1.56	2.25	1.82
WO4	1.15	7.04	8.18
WO6	1.73	0.31	2.04
BL2	3.38	5.96	9.33
BL4	4.08	16.49	20.57
BL1	13.14	0.87	13.99
BL3	----	2.75	2.75*
BL5	----	1.61	1.61*
BL7	----	2.10	2.10*
LP1	6.42	6.79	13.21
LP3	1.50	8.25	9.75
LP5	----	8.05	8.05*
LP7	----	2.50	2.50*
IW2	3.22	5.78	9.00
IW4	----	2.10	2.10*
IW6	2.64	2.60	5.24
SJ1	6.98	2.45	9.43
SJ3	0.30	1.66	2.96
SJ5	1.92	3.43	5.35
BY2	3.91	20.01	23.96
BY4	----	23.66	23.66*
BY6	----	1.50	1.50*
PF1	6.66	5.69	12.34
PF3	----	4.90	4.90*
PF5	3.11	7.06	10.17
PF7	----	0.80	0.80*
PC2	3.11	3.45	6.56
PC4	----	6.56	6.56*
PC6	0.49	12.56	13.05
IN1	0.21	6.67	6.88
IN5	----	8.50	8.50*
IN7	----	1.19	1.19*
RB1	----	1.81	1.81*
RB2	----	5.59	----

* Soluble phosphorus value below detection limit.

TABLE 9 (continued). AEROSOL INPUT--AUGUST

Filter number	Total soluble phosphorus, ng/m³	Total reactive phosphorus, ng/m³	Total available phosphorus, ng/m³
LT1	2.11	1.22	3.33
LT3	1.77	----	1.77**
LT7	5.64	1.76	7.40
WG2	0.95	7.06	8.01
WG4	3.87	10.62	14.49
WG6	8.04	4.10	12.14
BI3	1.20	2.84	4.13
BI5	3.99	0.64	4.63
BI7	7.91	0.21	8.12
B26	3.02	2.15	5.17
LP1	----	3.21	3.21*
LP3	0.37	0.96	1.32
LP5	6.83	3.68	10.51
LP7	16.83	3.51	20.34
IW2	0.32	0.58	0.89
IW4	----	2.31	2.31*
IW6	7.69	1.15	8.84
BJ1	18.92	12.20	31.12
BJ3	2.57	4.39	6.95
BJ5	4.91	5.13	10.04
BJ7	13.24	2.93	16.17
BY2	2.90	11.82	14.73
BY4	1.28	18.43	19.71
BY6	5.90	4.35	10.25
PF1	1.23	1.24	2.46
PF3	4.68	4.60	9.28
PF5	5.39	8.38	13.77
PF7	1.90	1.65	3.55
PC2	----	0.58	0.58*
PC4	----	3.25	3.25*
PC6	4.30	0.82	5.12
IN1	----	0.85	0.85*
IN3	1.17	2.66	3.83
IN5	6.47	2.19	8.66
IW7	1.71	----	1.71**
RR1	8.09	3.04	11.13

* Soluble phosphorus value below detection limit.
** Reactive phosphorus value below detection limit.

TABLE 9 (continued). AEROSOL INPUT--SEPTEMBER

Filter number	Total soluble phosphorus, ng/m³	Total reactive phosphorus, ng/m³	Total available phosphorus, ng/m³
LT1	11.27	6.61	17.88
LT3	19.94	9.36	29.30
LT5	19.18	8.97	28.15
LT7	7.21	1.33	8.54
WG2	22.88	10.55	33.43
WG4	23.18	7.77	31.15
WG6	13.53	6.14	19.67
BI1	10.63	10.64	21.27
BI3	11.66	6.13	17.79
BI5	15.63	5.53	21.16
BI7	3.54	1.55	5.09
BJ2	14.21	4.59	18.80
BJ4	20.85	5.89	26.74
BJ6	6.25	3.93	10.20
LP1	19.85	10.66	30.51
LP3	11.05	2.87	13.92
LP5	16.50	7.75	24.25
LP7	7.81	5.81	13.64
LN2	18.43	7.88	26.31
LN4	13.41	1.69	15.10
LN6	10.16	1.05	11.21
PC1	13.81	6.85	20.66
PC3	19.59	2.82	22.41
PC5	17.19	3.51	20.70
PC7	11.71	1.21	12.92
PF2	16.93	1.58	18.51
PF4	14.79	3.47	18.26
PF6	9.00	2.19	11.19
BY1	12.17	8.13	20.29
BY3	10.92	2.76	13.68
BY5	19.77	3.11	22.88
BY7	2.88	0.48	3.36
BJ2	28.91	3.30	32.21
BJ4	14.47	4.34	18.81
BJ6	9.79	1.60	11.39
LW1	7.35	10.09	17.44
LW3	9.96	4.42	14.38
LW5	16.78	6.86	23.64
LW7	4.53	1.50	6.03
RS1	9.14	7.42	16.56
RS2	9.57	6.10	15.67
RS3	10.23	6.77	17.00

TABLE 9 (continued). AEROSOL INPUT--OCTOBER

Filter number	Total soluble phosphorus, ng/m³	Total reactive phosphorus, ng/m³	Total available phosphorus, ng/m³
LT2	8.81	4.12	13.15
LT6	0.06	0.66	0.72
B12	1.98	----	----
B1A	15.73	7.02	22.75
W01	7.72	6.31	14.03
W05	2.14	4.39	6.53
W07	1.18	1.30	5.48
B21	8.41	4.62	13.03
B23	7.65	1.76	9.41
B25	5.21	4.19	9.40
B27	0.86	2.30	3.16
LP2	10.68	3.65	14.33
LP4	19.04	6.30	25.34
LP6	1.04	1.66	4.70
LW1	11.02	3.48	14.50
LW3	21.27	1.68	26.95
LW5	6.33	4.23	10.61
LW7	2.39	1.84	4.23
B32	7.71	2.96	10.67
B34	18.96	7.05	26.01
BY1	7.44	4.41	1.85
BY3	6.68	0.87	7.55
BY5	9.99	1.10	11.09
BY7	1.34	1.56	4.90
PE2	9.12	4.61	13.73
PE4	15.64	6.61	22.27
PE6	1.04	0.73	1.77
PC1	9.19	11.14	20.33
PC3	7.32	1.17	8.49
PC5	6.23	1.73	7.98
PC7	3.66	0.88	4.54
IB1	10.78	7.05	17.83
IB4	14.90	1.17	18.07
IB6	0.68	----	0.68**

** Reactive phosphorus value below detection limit.

TABLE 10. SIZE DISTRIBUTION OF PHOSPHORUS-CONTAINING PARTICLES, APRIL-SEPTEMBER 1975

Sample Month	Percent								
	>5.0μ	2.9-5.0μ	1.6-2.9μ	0.9-1.6μ	0.5-0.9μ	0.3-0.5μ	0.1-0.3	<1μ	<0.5μ
April	23.6	27.5	7.9	0.0	21.3	6.0	5.2	67.5	11.2
May	6.6	11.5	19.5	9.2	11.0	26.5	18.0	56.6	62.2
June	28.9	6.2	5.2	12.5	13.6	25.3	9.5	52.8	33.6
July	1.2	12.6	26.5	18.1	8.6	17.8	17.1	56.5	35.9
August	15.0	21.0	11.0	10.5	19.3	7.6	15.6	57.6	23.2
September	8.0	15.4	17.1	12.5	20.9	14.2	11.8	54.1	26.0
AVERAGE	13.9	15.7	14.2	11.9	15.8	15.7	12.8	55.7	28.5

that in almost all cases the stations located on the downwind shore collected a lower amount of aerosol than those on the upwind shore of Lake Huron. This observation is best illustrated by the month of June (Fig. 11). During the sampling period, the wind originated in the east and blew across the lake for four consecutive periods, turned south with no crosswind component for one period and then blew from the east for the last two sampling periods. Thus there were four periods during which the Canadian shore was upwind and two periods when the American shore was upwind. Except for the last Canadian upwind samples when the wind was swinging southward, the downwind stations observed a lower phosphorus content in the air, establishing that a definite cross-lake concentration gradient existed for the aerosol. To attempt to quantify this observation, one station on each shore was selected on a line parallel to the wind direction, and these samples collected at those stations were compared. In five cases (the first three Canadian upwind and the two American shore upwind) the ratio of downwind-to-upwind phosphorus contents of the aerosol, C/Co, was in the range of 0.4-0.8, even though rain occurred during two of these periods. Further, C/Co was independent of the magnitude of the concentrations, which ranged from an average of 13.4 to 33.2 $\mu g/m^3$. It was observed that the total average phosphorus was higher during the periods when the wind blew from the Canadian shore; however, this observation cannot be used to draw a definite conclusion on the effect of wind direction since this was not observed in most other months.

Although the effect of wind direction could not be determined, the effect of wind speed was found to be significant. When the ratio C/Co was plotted against wind speed (Fig. 12), it was observed that the ratio increased with increasing wind speed. In other words, the faster the wind blew, the smaller the fraction of the aerosol that fell out. Due to the decreased residence times of the aerosol over the lake at higher wind speeds, this effect is reasonable. These values of C/Co were then used to calculate deposition velocities for each period, using a simple mixing box model.

The assumptions made in the model used (Fig. 13) are: 1) a constant mixing height; 2) a complete sink at the bottom; 3) complete mixing of the components of the box; and 4) particles falling at some constant velocity. Under

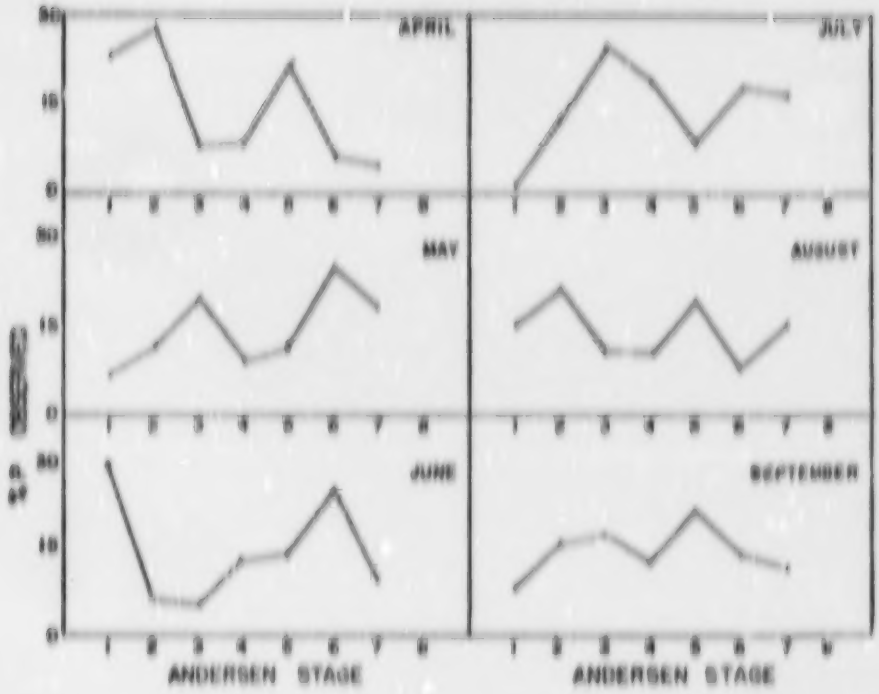


Figure 10. Size distribution of phosphorus in aerosol samples collected from April through September 1975. The size ranges for stages 1-7 are: >4.6 μ, 2.9-4.6 μ, 1.6-2.9 μ, 0.9-1.6 μ, 0.5-0.9 μ, 0.3-0.5 μ, and 0.1-0.3 μ, respectively.

these conditions, the equation for the deposition is:

$$\log(C/Co) = -kt = -\frac{Vd}{H}\,t$$

or

$$Vd = \log(C/Co)\,\frac{H}{t}$$

where Vd = deposition velocity
H = height of mixing layer
t = time between measurement of C and Co
C = downwind concentration
Co = upwind concentration

C and Co have been experimentally determined, H was determined from the aircraft data, and t can be determined by dividing the cross-lake distance by the wind speed. The only unknown, therefore, is the deposition velocity, Vd.

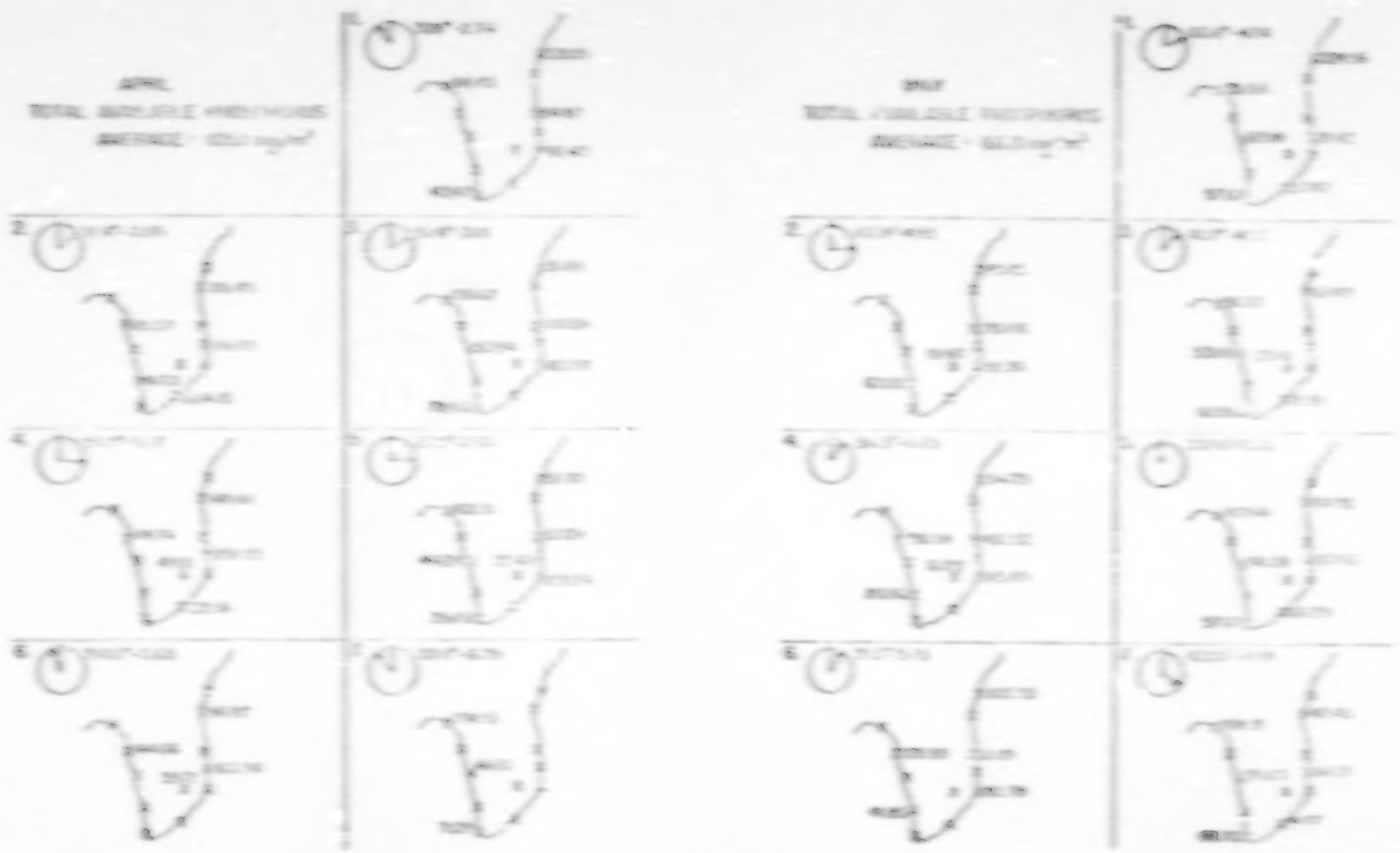
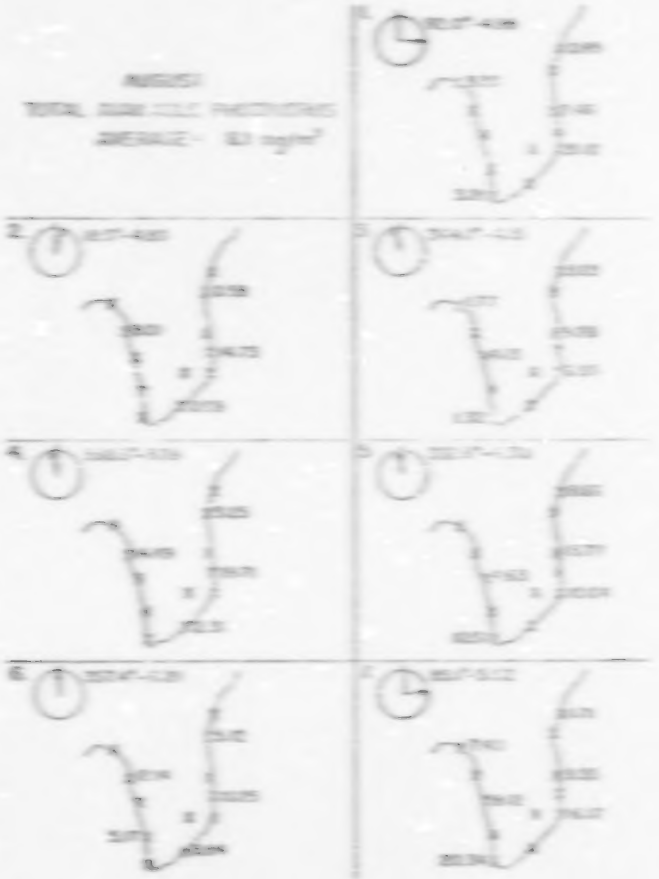
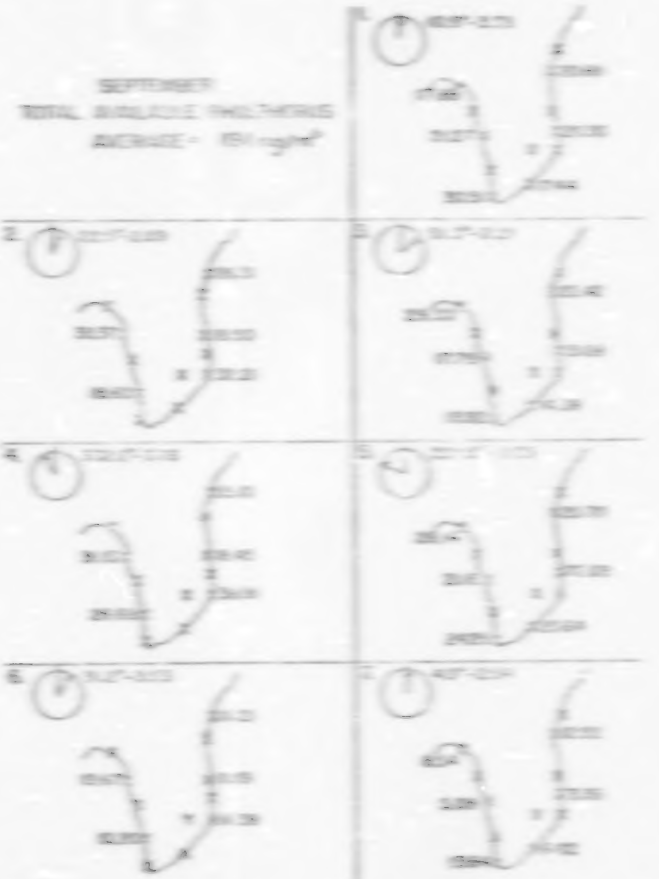


Figure 11. Plot of aerosol available phosphorus for each station, April-October 1975. Concentration is given in ng/m^3. The wind direction in degrees from north and wind speed in mph are indicated in the upper left corners for each sampling period.

Figure 11 continued.

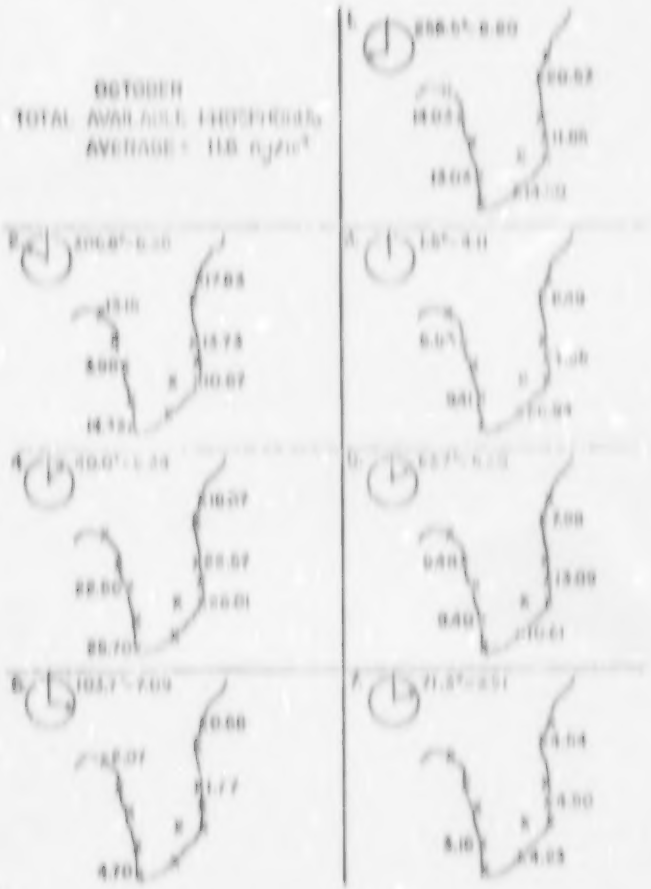


(c)



(d)

Figure 11 continued.



(g)

Figure 11 continued.

The calculation of deposition velocity at the various wind speeds is shown in Table 11. When the effect of residence time is removed from the C/Co relationship, it is observed that while the fraction deposited decreases with increasing wind speed, the deposition velocity of those particles actually increases (Fig. 14). The above results are consistent with the wind tunnel experiments of Sehmel and Sutter (1974). They observed that with monodisperse spherical particles of uranine (density = 1.5 g/cm^3) at temperatures from 15-22°C at wind speeds from 2.2 to 13.8 m/sec, the deposition velocity for particles greater than 1 μ increases with increasing wind speed over water surfaces. They observed that at any given wind speed, total deposition was a function of the concentration of particles above the surface (the more in the air, the more falls out), which agrees with our observation that C/Co is independent of the magnitude of the concentrations involved. The data for deposition over Lake Huron are the first field verification of

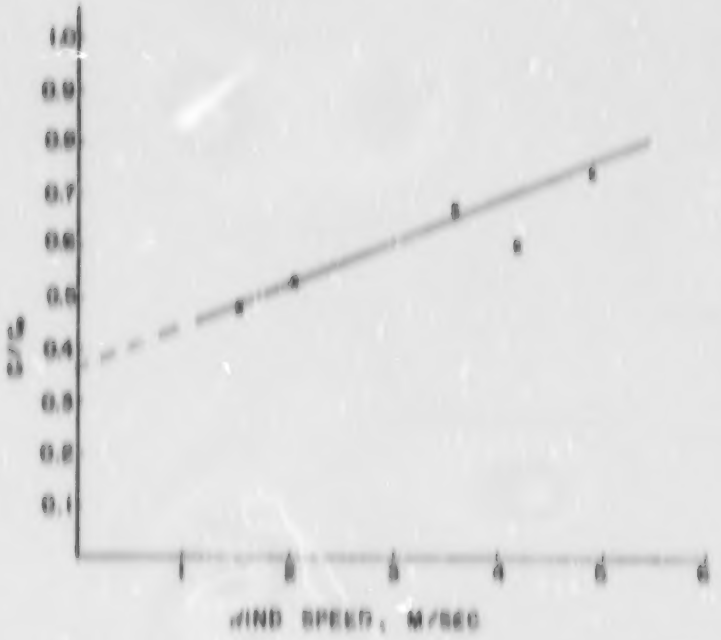


Figure 12. Deposition (C/Co) as a function of wind speed for total available phosphorus concentration, southern Lake Huron, June 1975.

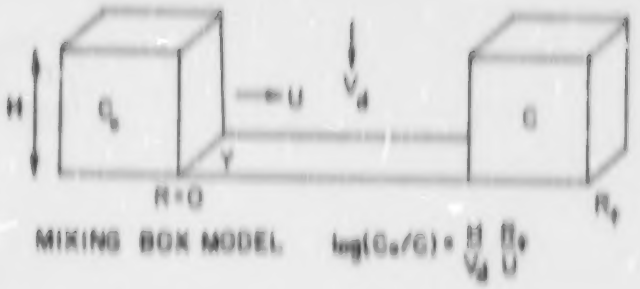


Figure 13. Schematic representation of mixing box model for particle deposition.

TABLE 11. CALCULATION OF DEPOSITION VELOCITY, Vd, AT VARIOUS WIND SPEEDS

Wind speed, m/s	C/Co	Vd^, cm/s
1.5	0.48	0.50
2.0	0.53	0.57
3.6	0.67	0.61
4.2	0.60	0.94
4.9	0.74	0.65

^Vd = (log Co/C) $\frac{H}{V}$ = (log Co/C) $\frac{H}{U}$

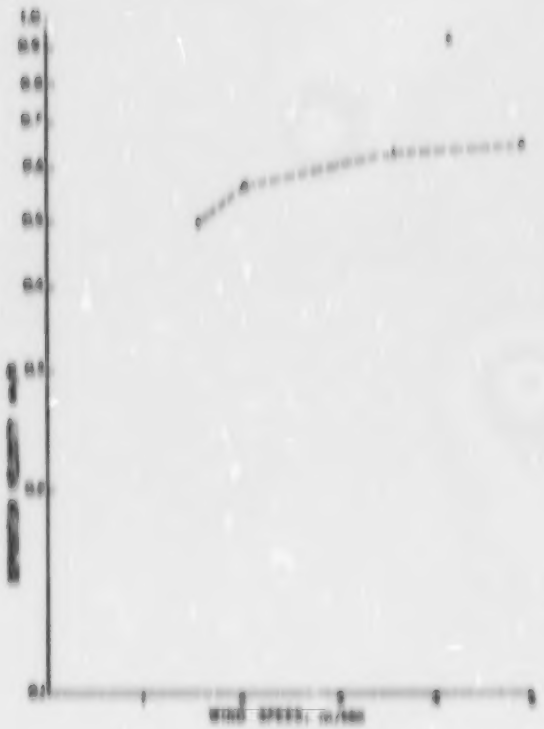


Figure 14. Deposition velocity, Vd, as a function of wind speed for total available phosphorus concentration, southern Lake Huron, June 1975.

the work of Schmel and Sutter, and in view of the number of variables involved in the samples, including heterogeneous particle size range, irregularly shaped particles, uncontrolled meteorological conditions, thermal gradients, particle density, etc. not present in the wind-tunnel data, the differences in actual deposition velocity between the two studies are not unreasonable. The field work gives a deposition velocity of the phosphorus-containing particles whose mean diameter is 1 μ to be 0.6 cm/sec, which is considerably higher than the value of 0.01 cm/sec from the wind-tunnel data.

SECTION 5

TOTAL AND RELATIVE INPUTS OF PHOSPHORUS FROM WET AND DRY DEPOSITION

From the above data, total and relative inputs of phosphorus to southern Lake Huron can be determined by comparison of the average deposition rates of wet, dry and total fallout (Table 12). The total deposition was determined by dividing the content of the total integrated samples by sampling time and surface area. Wet deposition was determined by multiplying the event rain concentration by the monthly volume of rain and dividing by the sampling period. Dry fallout was determined from the aerosol concentration and the deposition velocity.

WET DEPOSITION

Inputs due to wet deposition must be considered speculative due to the lack of a sufficient number of samples and incomplete analysis. The input of available phosphorus due to rainout and washout is estimated to be 76 metric tons, and the total phosphorus may be twice that value. Little emphasis was placed on this contribution during the present study; nevertheless, the values for rain concentration are comparable to other studies. Further, the estimated input of phosphorus agrees well with the value reported by Murphy

TABLE 12. WET, DRY, AND TOTAL AVAILABLE PHOSPHORUS DEPOSITION FOR THE MONTHS OF APRIL-OCTOBER 1975

Sampling period	Wet deposition[A]	Dry deposition	Total observed	% Wet	% Dry
4/18-5/12	-	5.0 ± 0.93	5.2 ± 5.8	-	96
5/16-6/9	-	2.7 ± 0.50	23.1 ± 4.6	-	12
6/13-7/7	1.7 ± 0.72	0.69 ± 0.31	5.3 ± 3.7	32	13
7/11-8/9	1.5 ± 1.1	0.41 ± 0.19	1.0 ± 0.22	148(?)	41
8/12-9/15	1.1 ± 0.49	0.71 ± 0.12	11.5 ± 2.8	9.6	6.2
9/19-10/8	0.12 ± 0.13	0.80 ± 0.12	2.9 ± 2.2	4.2	28
Average	1.1 ng/cm²/dy	1.7 ng/cm²/dy	6.5 ng/cm²/dy	15%	33%

[A] Soluble portion of available phosphorus only.

and Dookey (1975) for the input of phosphorus from precipitation to Lake Michigan. They estimate 1000 metric tons enter that lake in this manner. Correcting for the difference in surface area, the Lake Huron data would predict 900 metric tons. The greater input to Lake Michigan is undoubtedly due to the greater population density in the Lake Michigan Basin.

DRY FALLOUT

The average concentration of phosphorus in the aerosol was found to range from 0 to 369 ng/m^3 with an 8-month average of approximately 76 ng/m^3. Some typical values for the aerosol phosphorus concentration in other areas are: Los Angeles 1730 ng/m^3; Cincinnati 220 ng/m^3 (Athanassiadis 1969), southern Atlantic Ocean 20 ng/m^3[a]. Thus the value for the air over southern Lake Huron is considered low and typical of rural areas. Based on the data for aerosol phosphorus, the average deposition rate is 1.7 ng/cm^2/dy of available phosphorus. On a yearly basis, 59 metric tons of available phosphorus and almost 123 metric tons of total phosphorus enter southern Lake Huron from dry fallout.

The average total aerosol concentration, based on HiVol samples, is 27.6 µg/m^3. Rural values have been determined to vary from less than 30 to 150 µg/m^3 in other areas, with the usual value near the higher end of this range. Thus, based on aerosol concentration, the air over Lake Huron is relatively "clean." Using the HiVol data, total dry deposition has been calculated to be 0.60-5.7 µg/cm^2/dy with an average of 1.4 µg/cm^2/dy. This value agrees with a preliminary value of 1.7 µg/cm^2/dy obtained by Whelpdale (1974) based on samples collected in July 1968. Using the value of 1.4 µg/cm^2/dy, this amounts to an annual input of 49,000 metric tons of dry fallout to southern Lake Huron (surface area = 9.5 x 10^{13} cm^2).

TOTAL DEPOSITION

If all contributions to the total available phosphorus input are considered, a deposition rate of 6.9 ng/cm^2/dy was observed. Using this deposition rate, 235 metric tons of available phosphorus entered southern Lake Huron on a yearly basis. If only total available phosphorus inputs are considered, wet deposition accounts for approximately 34% of the amount observed in the integrated samples. Dry deposition accounts for 26% of the input to the lake surface. Thus at least 60% of the total available phosphorus can be accounted for by these two modes. Biological events and other local phenomena which can elevate the phosphorus content of the integrated samples accounts for most of the discrepancy. If the May-June integrated samples, which showed marked evidence of biological input, are eliminated, the wet-plus-dry inputs account for over 73% of the total available phosphorus observed. Such local events definitely result in an input to the lake but are local and restricted to nearshore regions. Thus the extrapolation of the deposition observed in integrated samples to a total lake input will be systematically high. This is especially true if one considers total phosphorus rather than total available phosphorus. Analysis of September-December 1975 samples showed that

[a] D.F.S. Natusch, Univ. of Illinois at Urbana-Champaign, pers. comm. 1975.

available phosphorus was 32 ± 16% of the total phosphorus observed. On a yearly input basis, 675 metric tons of phosphorus would be predicted to enter southern Lake Huron from the atmosphere, of which 152 metric tons can be accounted for from wet deposition and 123 metric tons from dry input. Thus only 41% of the total phosphorus input predicted from the integrated samples can be verified. Again, this discrepancy is believed to be due to biological and other local contamination of the integrated samples.

These values differ significantly from the only other work on atmospheric inputs to Lake Huron (Acres Consulting Services Ltd. 1975). The study areas differed somewhat in that the Acres work included an extra 3.7×10^{11} cm^2 of open lake and the 2.8×10^{11} cm^2 of Saginaw Bay. Probably as a result of inclusion of the relatively industrialized Saginaw Bay area, the value for total loading due to dry deposition was significantly higher (87,000 metric tons, corrected to southern Lake Huron area, as compared to 49,000 metric tons). The effect of industrial activity on the phosphorus content of rain and the total loading has been previously discussed. On the other hand, total phosphorus values obtained by analysis of integrated fallout samples gave a significantly lower estimated input (90 metric tons). The samples used to project this yearly input were collected during the period from October 1973 to July 1974. The winter months would be expected to predict lower inputs since the scavenging efficiency of snow is much less than that of rain (Murphy and Doskey 1975). The aerosol concentration in the air would also be expected to be lower due to snow cover.

LITERATURE CITED

Acres Consulting Services Ltd. 1975. Atmospheric loading of the upper Great Lakes. Canada Centre Inland Waters, Burlington, Ont., Vol. 2. 126 p.

Andersen, A. A. 1966. A sampler for respiratory health hazard assessment. Am. Ind. Hyg. Assoc. J. 27: 160-165.

Athanassiadis, Y. C. 1969. Preliminary air pollution survey of phosphorus and its compounds. A literature review. U.S. Public Health Service, Raleigh, North Carolina, Pub. No. APTD 69-45.

Bannerman, R. T., D. E. Armstrong, R. F. Harris and G. C. Holdren. 1975. Phosphorus uptake and release by Lake Ontario sediments. U.S. Environmental Protection Agency, Grosse Ile, Michigan, Rep. No. EPA-660/3-75-006.

Bowen, H. J. M. 1966. Trace elements in biochemistry. London: Academic Press. 196 p.

Elder, F. C. 1975. International Joint Commission Program for Atmospheric Loading of the Upper Great Lakes. Paper presented at Second Interagency Committee on Marine Science and Engineering Conference on the Great Lakes, Argonne, Ill.

Lee, R. E., Jr. and R. Goranson. 1972. Cascade impactor network. National Environmental Research Center, Research Triangle Park, North Carolina, Pub. No. AP-108 (PB 213177/5).

Menzel, D. W. and N. Corwin. 1965. The measurement of total phosphorus in sea water based on the liberation of organically bound fractions by persulfate oxidation. Limnol. Oceanogr. 10: 280-282.

Miller, W. E., T. E. Maloney and J. C. Green. 1974. Algal productivity in 49 lake waters. Water Res. 8: 667-679.

Murphy, J. and J. P. Riley. 1962. Modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27: 31-36.

Murphy, T. J. 1974. Sources of phosphorus inputs from the atmosphere and their significance to oligotrophic lakes. Univ. Illinois, Water Resources Research Center, Urbana, Rep. No. 92.

_____ and F. V. Doskey. 1975. Inputs of phosphorus from precipitation to Lake Michigan. U.S. Environmental Protection Agency, Grosse Ile, Michigan, Rep. No. EPA-600/3-75-005.

Portelli, R. In press. Mixing heights, wind speeds and air pollution potential for Canada. Atmosphere.

Puraglove, J., Jr. 1967. Fly ash in 1980. Coal Age, Aug. 1967, pp. 84-85.

Schelske, C. L. and E. F. Stoermer. 1971. Eutrophication, silica depletion and predicted changes in algal quality in Lake Michigan. Science 173: 423-424.

_____ and _____. 1972. Phosphorus, silica, and eutrophication of Lake Michigan, p. 157-171. In G. E. Likens (Ed.), Nutrients and eutrophication. Lawrence, Kansas: Allen Press.

_____, L. E. Feldt, N. A. Santiago and E. F. Stoermer. 1972. Nutrient enrichment and its effect on phytoplankton production and species composition of Lake Superior. Proc. 15th Conf. Great Lakes Res., pp. 149-165.

Schmel, G. A. and S. L. Sutter. 1974. Particle deposition rates on a water surface as a function of particle diameter and air velocity. J. Recherches Atmospherique 8: 911-920.

Whelpdale, D. M. 1974. Particulate residence time. Water, Air and Soil Pollution 3: 293-300.

APPENDIX--SAMPLING STATION LOCATIONS

Lighthouse County Park (LT). Permission to use this facility was granted by the Board of County Road Commissioners of Huron County, Mr. Lester Ender, Chairman. The park is located near Huron City, Mich., approximately 0.8 km from M-25 directly on the lake shore. A 5-m mast was attached to a lightpole in a grassy clearing removed from obstructions, approximately 150-200 m from the shore. Little automobile traffic was observed in this area of the park. The sampler was relocated twice, once due to objections to the noise and once due to contamination from a nearby building. The station was located at 44° 01.4' N and 82° 47.3' W.

Wagener County Park (WG). This park, 6.4 km south of Harbor Beach, Mich., on M-25, was also under the supervision of the Huron County Road Commission. The park is a day-use area and a season trailer park with no tenting, therefore campfires were not a problem. The sampling area was located at the end of the park at the shoreline, where the 5-m mast was attached to a power pole. A number of tall trees were located near the sampler and may have interrupted normal air flow. The soil is rock and sand. The station was at 43° 47.7' N and 82° 38.0' W.

Sanilac County Park #1 (SI). Mr. Dale Wheeler, Board of County Road Commissioners of Sanilac County granted permission to use this park and Sanilac #2. The park is 4 km north of Forester, Mich., on M-25 and is a day-use and season trailer park, a park manager is in permanent residence at the park. The 5-m mast was anchored to a wooden post on the edge of the beach area. Power was supplied from a building nearby. The beach area is designated for picnics only, and although charcoal grills were located within 25 m of the sampler they were not observed to be in use during any of the sampling trips. The latitude and longitude of this station were 43° 30.7' N and 82° 35.6' W.

Sanilac County Park #2 (S2). This day-use only park is located about 6.4 km north of Lexington, Mich., on M-25. The mast was anchored to a stairway leading from the 5-m bluff to the beach. The sampler was removed from all obstruction and 50 m from the caretaker's summer residence. The location of this station was 43° 17.7' N and 82° 32.8' W.

Lakeport State Park (LP). Permission to use this park was granted by Mr. Paul Reavick, Michigan Department of Natural Resources, and the park manager Mr. J. Janke. The park is located at the town of Lakeport, Mich., on M-25. The mast was attached to a pumphouse approximately 100 m from the shore in the day-use area. A stand of trees was located between the sampler and the shore; soil was grass-covered and the main road, M-25, was located 250 m

from the station across an open field which was a potential source of contamination. The latitude and longitude of the station were 43° 04.8' N and 82° 30.0' W.

Ipperwash Provincial Park (IW or IP). Permission to use the three provincial parks was granted by Mr. W. H. Charlton, Regional Director of the Ministry of Natural Resources, Ontario, and the individual park managers. The park extends along the shore at Kettle Point about 3.4 km west of Ont.-21 near Ravenswood, Ont. The 5-m mast was located in a 100 x 50 m clearing, attached to a 2.5-m tall pumphouse. The clearing is on a 5-m bluff behind a low stand of pine trees, and the soil is mainly sandy and grass-covered. The location of this station was 43° 13.0' N and 82° 00.9' W.

St. Joseph Shores on Lake Huron (SJ). This station was located on private property owned by Mr. Frank Moore, Zurich, Ont. It was located 2.4 km south of the St. Joseph intersection on Ont-21, on a point well past the end of a private paved drive and at least 200 m from the only residence in the immediate area. The sampler was attached 5 m up a 50-m tower used for television reception. The tower itself was located on a 10-m cliff at the edge of the lakeshore at the end of a well-groomed lawn. The latitude and longitude were 43° 24.5' N and 81° 43.1' W.

Bayfield Marina (BY). Permission to use this facility was granted by Mr. R. E. Snead, Small Craft Harbour Branch, Environment Canada, and by Mr. Tom Castle, the marina operator. The marina is located at the mouth of a river at Bayfield, Ont. Due to the need for electric power, the mast was attached to the side of a service building approximately 3 m tall. A dirt road leading from the main road into the marina was approximately 5 m away but not well travelled. The sampler was 100 m from the lakeshore, located at approximately 43° 34.1' N and 81° 42.7' W.

Point Farms Provincial Park (PF). The park is 7 km north of Goderich, Ont., on Ont-21. The mast was attached to a comfort station on the beach, about 0.8 km from the main road. The beach area is at the bottom of a tree-covered 20-m bluff and the sampler was 30 m from the lakeshore. The area was designated as day-use and no campfires were permitted in the area. The latitude and longitude of this station were 43° 48.4' N and 81° 43.6' W.

Point Clark Boat Club (PC). The board of directors of this private boat club granted permission to establish a sampling station on their property. The sampler was attached 5 m up a power pole with an angle brace and eye hook. It was directly on the lakeshore on a point of land removed from all structures. The nearest residences were summer camps approximately 100 m away. The only road was a access ramp to the water owned by the private club and not heavily travelled. A potential source of contamination was a nearby marine fuel storage tank (150 gal). The station was located at 44° 04.8' N and 81° 46.0' W.

Inverhuron Provincial Park (IN). The park is located at Douglas Point about 3 km west of Tiverton, Ont. The 5-m mast was attached to a comfort station located at lake level in a sandy beach at the south end of the park. The area was day-use only and removed from the camping area. A nearby parking

lot was a potential source of contamination, but was seldom in use. The proximity of this station to the Bruce Nuclear Power Development raised the question of contamination from the oil-fired power plant which supplements the reactor facility. No evidence for this contamination has been observed, however. This station was located at 44° 17.7' N and 81° 36.3' W.